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A REGENERATIVE LIMESTONE PROCESS FOR FLUIDIZED-BED COAL COMBUSTION AND DESULFURIZATION

R. C. Hoke, et al

Esso Research and Engineering Company

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A REGENERATIVE LIMESTONE PROCESS FOR FLUIDIZED-BED COAL COMBUSTION AND DESULFURIZATION

by

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16. Abstracts **The report gives results of an experimental study of the pressurized combustion of coal in a fluidized bed of limestone and regeneration of sulfated limestone. The study is part of a program to develop fluidized-bed coal combustion as a means of desulfurizing flue gas in-situ and generating clean power at low cost. The process, including regeneration of spent limestone by reduction to lime, produces a gas stream containing a sufficient concentration of SO2 to be fed to a by-product sulfur recovery unit. The combustion runs were limited by operating problems, especially plugging in the coal injection line. Initial SO2 removal rates were about 85%; however, attrition rates were high with one SO2 sorbent, Tymochtee dolomite. The regeneration step was studied at pressures up to 10 atm and temperatures up to 2100°F. SO2 concentrations measured in the product gas averaged about 2% at 10 atm and 2100°F, or about 40% of the concentrations calculated by assuming equilibrium between the solids and regenerating gas. High conversion of sulfated material to lime was achieved by injecting air into the bed, by forming adjacent reducing and oxidizing zones, and by minimizing formation of undesired CaS.**

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ABSTRACT

An experimental study was begun of the pressurized combustion of coal in a fluidized bed of limestone and regeneration of sulfated limestone.

The work is part of an overall program aimed at developing fluidized bed coal combustion as a means of desulfurizing flue gas in-situ and generating clean power at low cost. The process includes regeneration of spent limestone by reduction to lime. This produces a gas stream containing a sufficient concentration of SO_2 to be fed to a by product sulfur recovery unit.

The regeneration step was studied at pressures up to 10 atm and temperatures up to 2100°F. SO_2 concentrations measured in the product gas averaged about 2% at 10 atm pressure and 2100°F, about 40% of the concentrations calculated by assuming equilibrium between the solids and regenerating gas. High conversion of sulfated material to lime was achieved by injecting air into the bed, forming adjacent reducing and oxidizing zones, and minimizing formation of undesired CaS.

Combustion studies also began. The combustion runs were limited by operating problems, especially plugging in the coal injection line. Initial SO_2 removal rates were about 85%. However attrition rates were high with one SO_2 sorbent, Tymochtee dolomite.

This report was submitted in fulfillment of Contract CPA 70-19 by Esso Research and Engineering Company under the sponsorship of the Environmental Protection Agency. Work was completed as of July 31, 1973.

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SECTION I

CONCLUSIONS

The regeneration of $CaSO_4$ to CaO and SO_2 appears to be limited by reaction rates. The measured SO_2 concentration in the product gas from the regenerator averaged about 40 to 50% of the maximum concentration calculated by assuming the solids and gases were in chemical equilibrium. At 10 atm* pressure, the measured SO_2 concentration averaged around 2%. Additional work will be necessary to determine if conditions can be found to allow a closer approach to equilibrium. Two routes could be followed - improving the quality of fluidization and increasing the gas/solids residence time.

High conversion of $CaSO_4$ to CaO was obtained by adding auxiliary air directly to the fluidized bed. This created adjacent reducing and oxidizing zones in the bed and reduced the tendency to form undesired CaS. Addition of a portion of the fuel normally used in the regenerator reducing gas generator directly to the fluidized bed produced higher and more uniform bed temperatures without causing bed agglomeration.

Of the SO_2 released by the combustion of coal, 85 to 90% was retained by the fluidized bed when calcined limestone or half-calcined dolomite was used as the bed material at 5-8 atm pressure. However, the runs were very short because of plugging in the coal injection probe. Longer runs are necessary before definite conclusions can be drawn about the suitability of the limestone or the dolomite. The dolomite (Tymochtee) gave very high attrition rates and may not be suitable for once-through operation.

Feeding of coal using a modified Petrocarb pneumatic injector at 10 atm pressure and low feed rates is possible. However, careful attention must be paid to operating conditions to prevent plugging of the injection lines. Additional modifications to the probe design are being made to reduce further coal plugging in the injection probe.

A number of equipment developments have been made including the design and construction of a very versatile burner used to generate heat and reducing gas for the regenerator. The burner can be operated over a wide range of pressures, flow rates and oxidizing or reducing conditions. A water cooled fluidizing grid was also developed which operates in the presence of very high gas temperatures in the regenerator.

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* EPA policy is to express all measurements in Agency documents in metric units. Because implementing this practice will result in undue cost, NERC/RTP is providing conversion factors for the particular non-metric units used in this document. For this report these factors are located on page 95.

SECTION II

RECOMMENDATIONS

Work in the area of fluidized bed coal combustion should proceed along two lines. First, work on a non-regenerative pressurized combustion system should proceed at this time to speed application of fluidized bed combustion and prevent any delays which could result from the development of a regenerative system. Second, work on the regeneration step should proceed as rapidly as permitted by the availability of funds, to develop a process which would minimize the disposal burden of spent limestone.

It is recommended that the pressurized coal combustion program should first concentrate on the solution of the remaining operational problems. The effect of precalcination of a typical limestone and dolomite on SO_2 removal should then be studied. This would be done to study further the effects of precalcination conditions on stone capacity recently reported by Westinghouse Research Laboratory. A study would then be made of the effect of operating conditions on desulfurization effectiveness, NO_x and trace emissions, attrition and utilization of the sorbent, combustion efficiency and heat transfer rates. The operating conditions studied would include pressure, temperature, bed depth, fluidizing velocity and excess oxygen. This study should be made with several combinations of coals and sorbents (stones). Suggested coals are Eastern, Western and possibly lignite.

The regeneration program should be based on the use of sulfated limestone or dolomite rather than pure $CaSO_4$. The study should determine the effects of improving fluidization quality and increasing gas residence time on the SO_2 product concentration and the effect of repeated combustion/regeneration cycles on the activity of the recycled limestone or dolomite.

The fluidized bed combustion unit could be used further to screen other coals and sorbents and possibly even shale. It could also be run in conjunction with the fluidized bed Miniplant to guide the selection of operating conditions for the Miniplant and to help resolve problems arising from the operation of the Miniplant.

SECTION III

INTRODUCTION

The fluidized bed combustion of coal is a new combustion technique which can reduce the emission of SO_2 from the burning of sulfur-containing coals. This is done by using limestone or dolomite as the bed material. This technique has other potential advantages over conventional coal combustion systems which could result in a more efficient, less costly method of power generation. High heat transfer coefficients between the fluidized bed and immersed steam generation surfaces reduce the steam tubing requirements, and also permit operation at lower and more uniform bed temperatures, in the vicinity of 1500 to 1700°F. The lower temperatures also reduce NO_x emissions and decrease steam tube corrosion. Lower grade coals can also be burned since the bed temperatures are lower than ash slagging temperatures.

In the fluidized bed boiler, limestone or dolomite is calcined and reacts with SO_2 and oxygen in the flue gas to form $CaSO_4$ as shown in reaction (1). When used on a once-through basis, high limestone or

$$CaO + SO_2 + 1/2O_2 \longrightarrow CaSO_4 \qquad (1)$$

dolomite feed rates to the boiler are required if SO_2 removal of 90% or more is to be achieved. In order to reduce the solid waste disposal burden created by high limestone feed rates, a system is now under study in which the $CaSO_4$ would be regenerated back to CaO in a separate fluidized bed reactor by reaction with a reducing gas at a temperature of about 2000°F as shown in reaction (2). The regenerated CaO would be

$$CaSO_4 + \overset{CO}{H_2} \longrightarrow CaO + SO_2 + \overset{CO_2}{H_2O} \qquad (2)$$

returned to the boiler where it would again react with SO_2 and O_2.

Engineering and cost analyses carried out by Westinghouse Research Laboratory for the Environmental Protection Agency (EPA) indicated a greater commercial potential for a pressurized combustion system when used in conjunction with a combined gas-steam turbine power generating plant. Based on these analyses, EPA requested Esso Research and Engineering Company to study the combustion and regeneration steps at pressures up to 10 atm. A new pilot plant capable of operating at these conditions was built and operated. The primary purpose of the pilot plant study was to explore the effect of operating parameters on combustion and regeneration at pressures up to 10 atm. In addition, the study was to include measurement of the activity maintenance of limestone or dolomite due to repeated combustion, regeneration cycles. Measurement of emission of trace elements from coal combustion was also to be made. Development and testing of equipment and operating procedures was also carried out as part of the program. A test program

for the operation of the large fluidized bed coal-combustion Miniplant was also developed as part of the program. In addition, a small amount of work was done in the cold model fluidization test unit to study fluidization characteristics and transfer of solids between the combustion and regenerator vessels. This was done in support of the Miniplant unit construction effort. A short laboratory program was also carried out in small fixed bed units studying the reduction of NO by CO under simulated combustion conditions. Some fixed or semi-fluidized bed regeneration studies were also carried out in small laboratory equipment.

SECTION IV

EXPERIMENTAL EQUIPMENT, MATERIALS, PROCEDURES

COLD MODEL TEST UNIT

For the purpose of verifying the design of the pulsed air solids transfer system used in the design of the fluidized bed coal combustion Miniplant, and to permit visual observation of its fluidization characteristics, a cold model test unit (CMTU) was built. The CMTU is a two vessel fluidized solids system constructed from Plexiglas, a transparent acrylic plastic. The CMTU was designed to operate at ambient temperature and pressures up to 60 psig.

Figure 1 is a picture of the CMTU. The unit consists of two 5.5 inch I.D. vessels simulating the combustor and regenerator of the Miniplant. The simulated combustor (i.e., the vessel on the left in Figure 1) is 18 feet tall and was assembled from three flanged sections. The regenerator is made of two flanged sections and stands 12 feet tall. Both vessels have bottom plenum chambers and grids for distributing the fluidizing air and single stage aluminum cyclones for removing entrained solids. These solids can be returned to the fluidized beds or collected as desired.

Nylon reinforced transparent PVC hose, 1.5 inch I.D. is used for solids transfer between the two vessels. This permits visual observation of solids movement in these lines which connect the upper part of the vessel transferring the solids to the lower part of the vessel receiving them. The small receiving-injection pots to which the bottom of these lines are attached are equipped with fluidizing and pulsed air. In some of the solids transfer studies, the use of an overflow collector was investigated as a means of creating an enlarged solids reservoir in the transmitting vessel. In the Miniplant, such a reservoir would serve to insure a continued solids seal in the transfer legs and minimize backflow of gases between reactors. The enlarged reservoir, shown on the regenerator vessel in Figure 2, was constructed of a 6 inch I.D. aluminum tee with a plate on the inside to serve as a solids baffle and a Plexiglas window on the outside for observation of the solids.

In addition to studying solids transfer techniques, the CMTU was used to determine what effect the hair pin heat transfer loops designed for the Miniplant would have on the fluidization characteristics of the combustor. Figure 3 shows a simulated heat transfer loop section that was used in the CMTU. It was fabricated of 3/8 inch aluminum as a prototype half-scale version with the same configuration and pitch as the Miniplant design. It is 68 inches in vertical length starting at a point 13.5 inches above the distributor grid. Insertion of the coil reduces the average cross section area by 8%.

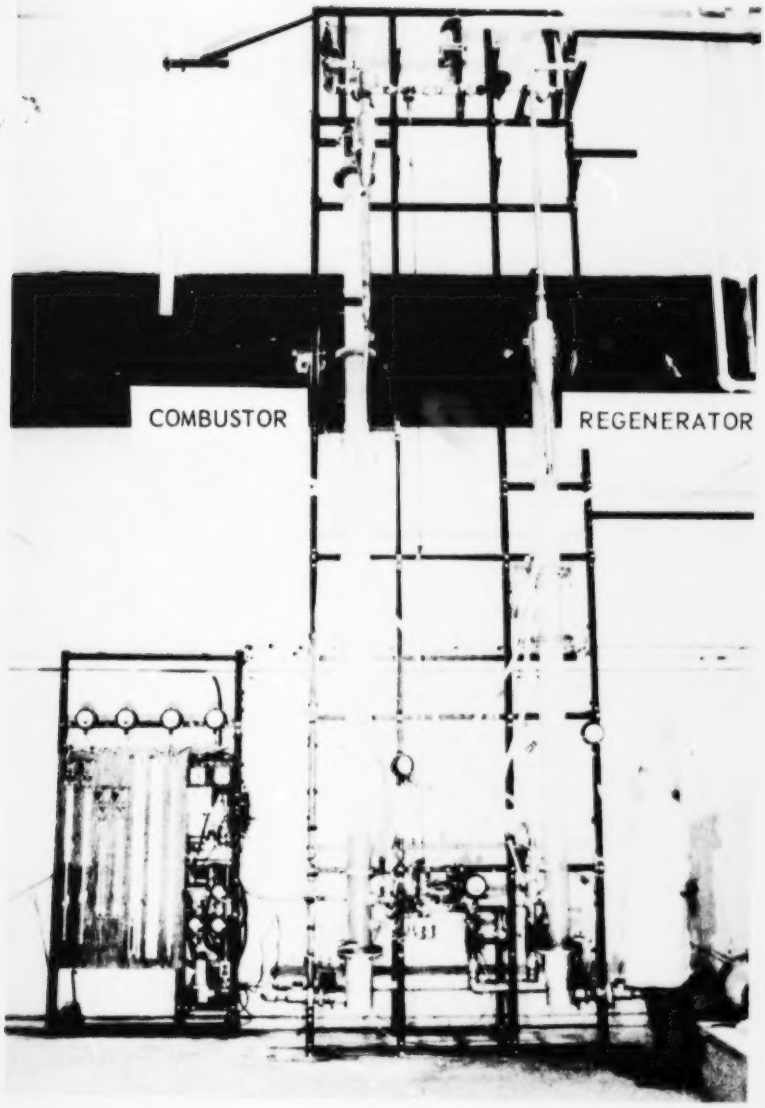


Figure 1. Cold model test unit

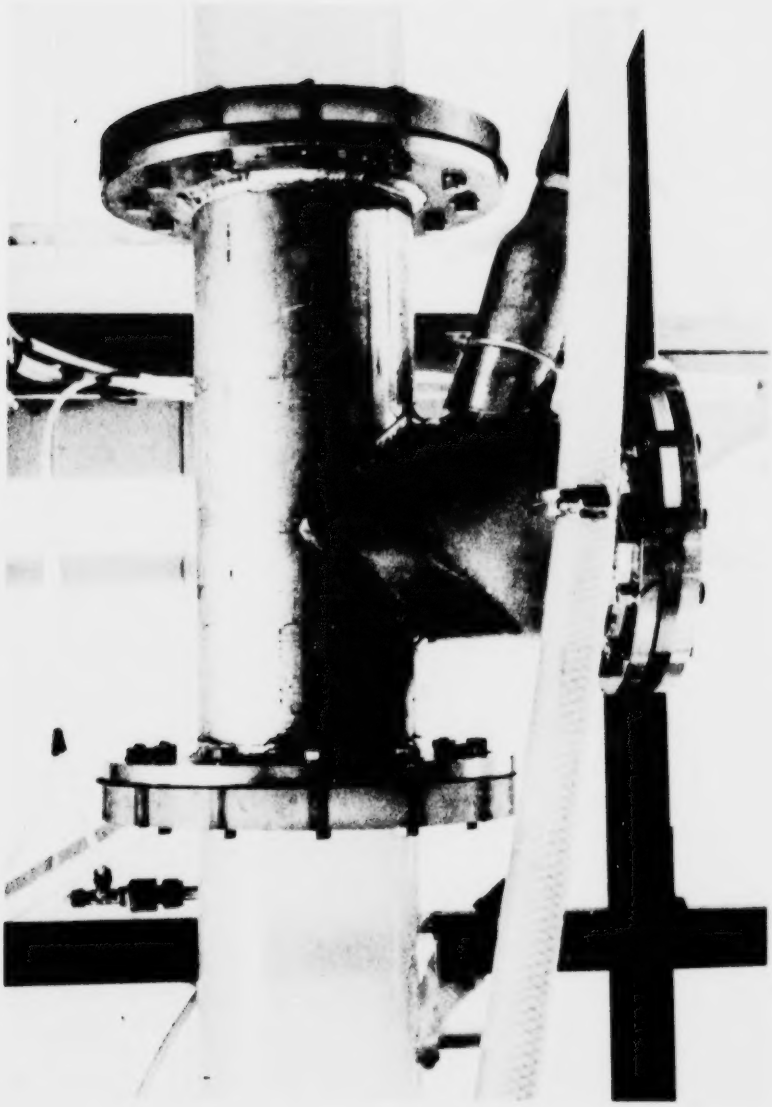


Figure 2. Cold model test unit solids reservoir

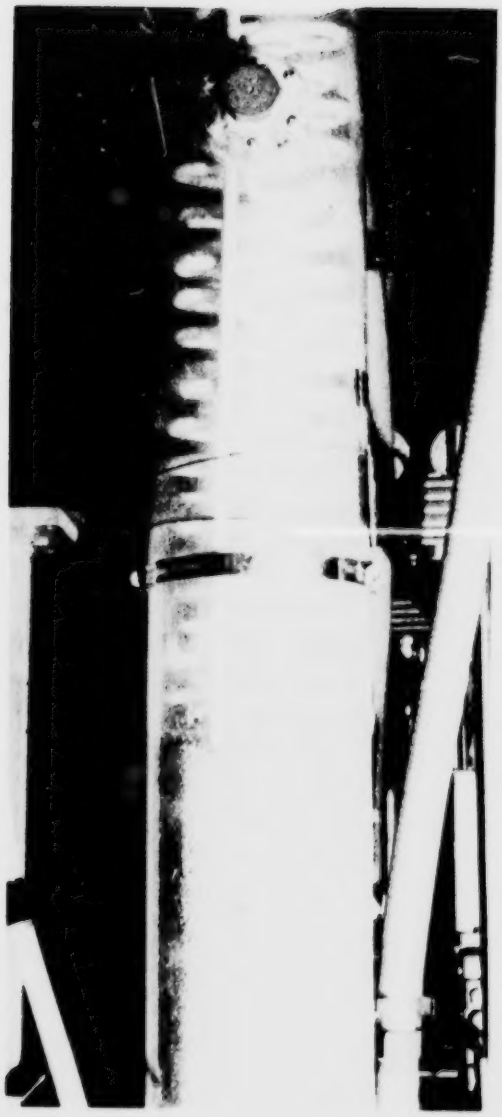


Figure 3. Cold model test unit simulated heat transfer coils

Gas flow rates to each of the two reactors of the CMTU could be varied. A control panel situated to the left of the Plexiglas vessels permitted measurement of their flow rates and of their individual bed pressure drops. It also controlled and measured the pressure differential between beds, and provided a means of varying the on-off pulsing times and the air flow rates for the solids transfer pots.

FLUIDIZED BED COAL COMBUSTION UNIT

A schematic diagram of the Esso fluidized bed combustion unit is shown in Figure 4. The primary components of the unit are (1) the coal feeding system, (2) the fluidized bed combustor, (3) and the gas handling and analytical equipment.

Coal Feeding Equipment

Figure 5 shows the Petrocarb Model 16-1 ABC injector. The main features are a conical-bottom tank that holds solids to be fed and an orifice and mixing valve assembly that mixes solids with carrier gas. Solids in the tank are aerated by a controlled stream of air at a selected pressure. Aerated solids flow through the orifice at the bottom of the tank into the mixing valve assembly and are picked up by a controlled stream of carrier gas (air). Solids are pneumatically conveyed through a transport line into the receiving vessel. The feed rate of solids is controlled by pressure in the feed tank, carrier or injection air flow rate, and pressure differential between the feed tank and receiving vessel.

The Petrocarb solids feeder shown in Figure 5 was modified to feed powdered coal (-30 mesh) at rates of 6-28 lbs/hr into the combustor against pressures of up to 10 atm. The feeder, as it is supplied by Petrocarb, can handle only much higher feed rates. The diameter of the orifice was reduced to 3/16 inch and the Petrocarb injection hose was replaced with a 1/4 inch diameter (O.D.) x 15 feet long stainless steel tube. In order to make the feeder work satisfactorily with the batch combustor, the feeder to combustor presssure differential had to be held constant. This was accomplished with automatic controls which maintained the pressure in the feed tank above the pressure in the combustor by the desired amount. A summary of the coal feeder test program and a detailed description of the modifications made on the Petrocarb injector are given in Section V.

Fluidized Bed Combustor

A schematic diagram of the fluidized bed coal combustor is given in Figure 6. The vessel was constructed from four sections of 10 inch standard wall carbon steel pipe and refractory lined with Grefco Litecast No. 7528 to an inside diameter of 4 inches. The height of the vessel, above the fluidizing grid, was about 16 feet. Below the grid was a 2 foot long burner section lined with Bubbalite. The fluidizing grid, which was made of stainless steel, had seven air distributor caps

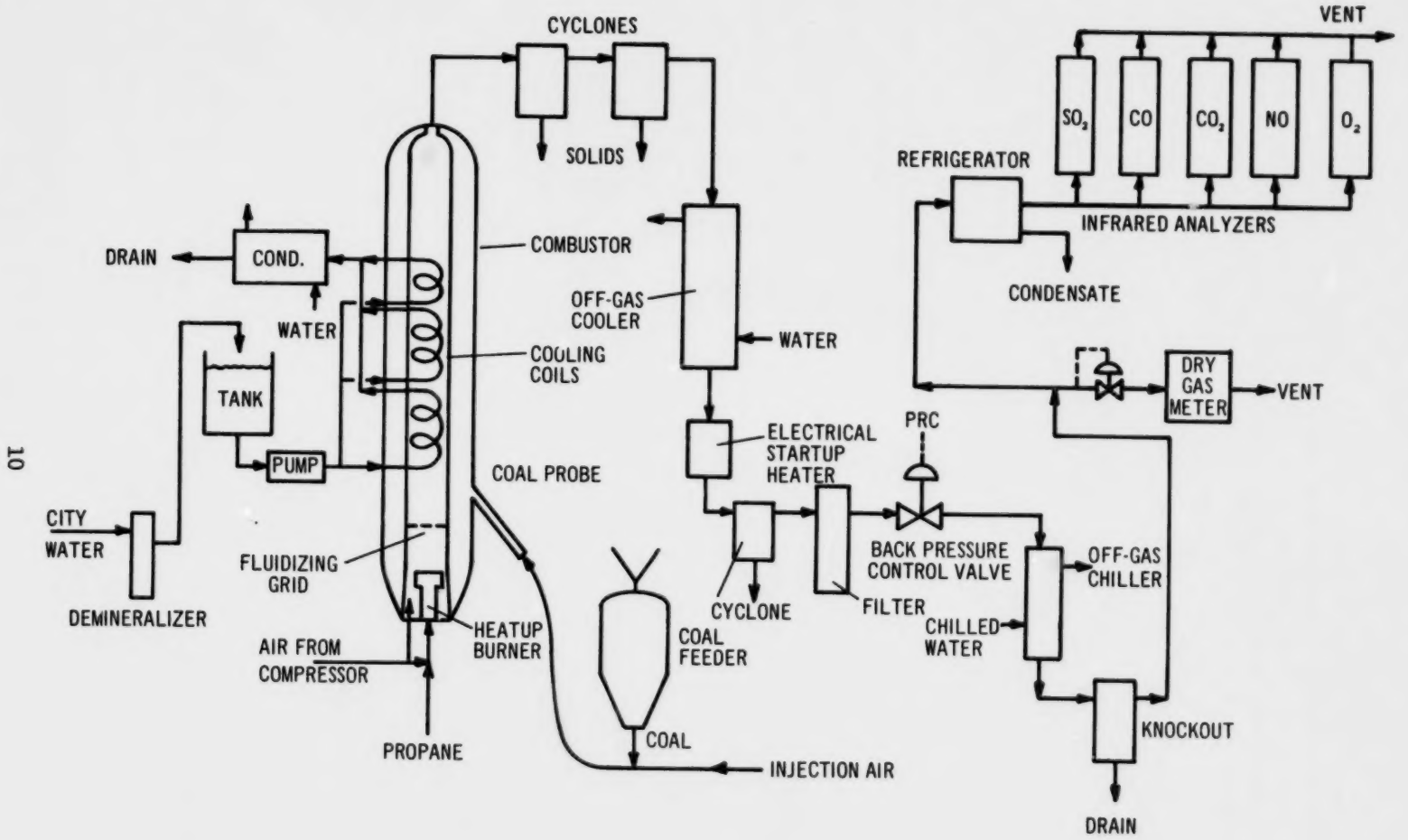


Figure 4. Fluidized bed coal combustion unit

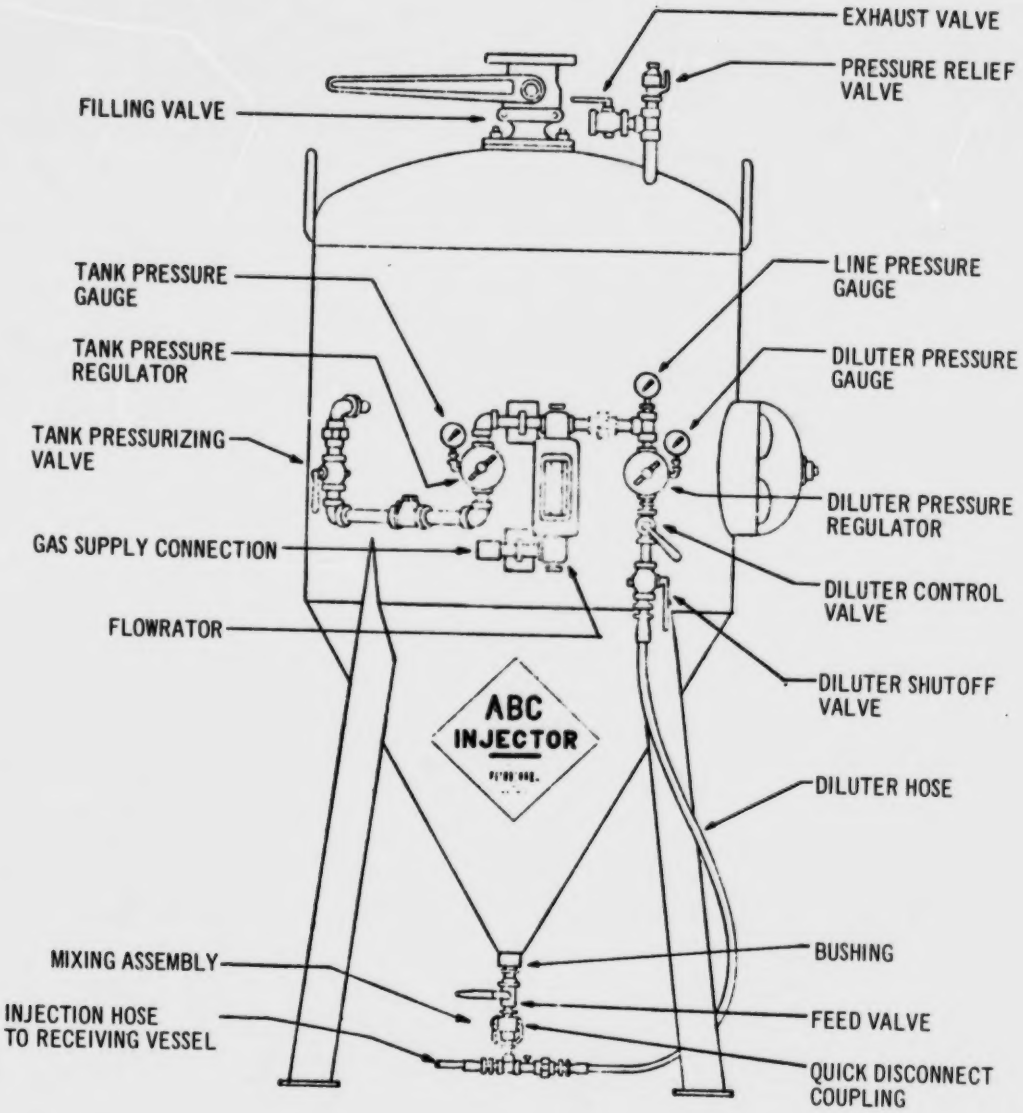


Figure 5. Petrocarb coal injector

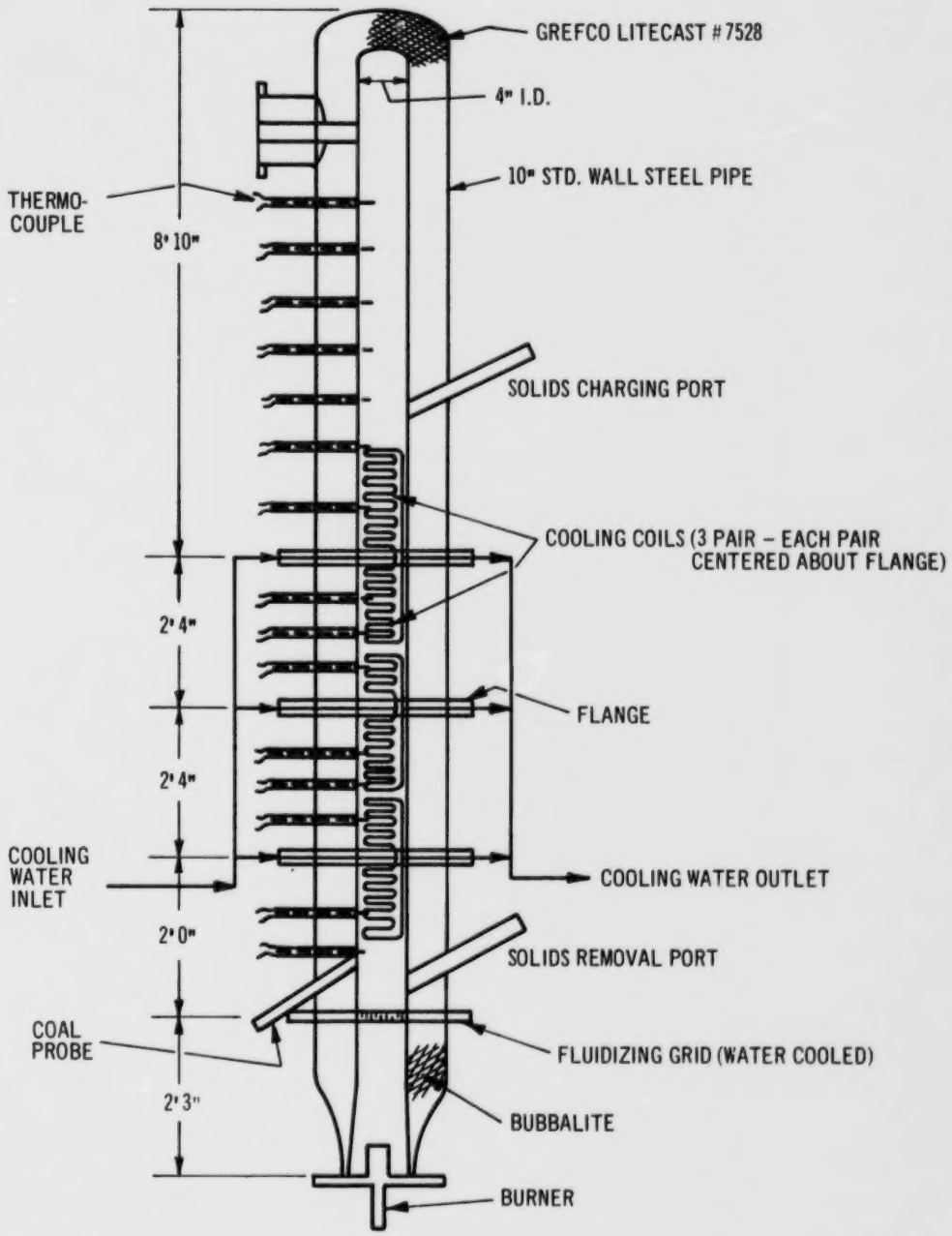


Figure 6. Fluidized bed coal combustor

and was water-cooled. It is described in Figure 7. A propane burner, located at the bottom of the burner section, was used to preheat the unit to above the self-ignition temperature of coal. The burner is described in more detail in Section V. The maximum operating temperature and pressure of the batch combustor were 1900°F and 10 atm., respectively. Two air compressors supplied sufficient air for operation at a superficial velocity of 6 ft/sec at 10 atm and 1600°F (about 80 SCFM).

Bed temperature was controlled by three pairs of serpentine wound cooling coils made of 1/4 inch diameter stainless steel tubing. The total surface area was about 6.3 sq. ft. The center of each pair of coils was located at a flange in the shell of the combustor. Water flowed in parallel to each of the six coils; flow rate to the lower and upper pair of coils was manually controlled but flow to the center pair was automatically controlled to give the desired bed temperature. Thermocouples were located 6 inches apart in the lower sections of the combustor and 12 inches apart in the upper section.

Solids were loaded into the combustor through a charging port located in the upper section. Solids could be removed through a port in the lower section or, alternatively, transferred directly to the regenerator by blowing them through a 2 inch pipe supplied for this purpose.

Coal entered through a water-cooled coal injection probe to which was connected the end of the 15 feet x 1/4 inch diameter coal injection tube. The probe was a 14 inch length of the 1/4 inch diameter stainless steel tubing surrounded by a jacket through which cooling water flowed.

Gas Handling and Analytical System

Flow of air and fuel into the combustor, and system pressure, were under automatic control. Gases leaving the combustor first passed through two cyclones, which removed entrained solids and fly ash. An off-gas cooler, which followed the cyclones, reduced the temperature of the off-gas to the desired level. The off-gas then entered an expansion coil of 1 inch diameter stainless tubing which was electrically heated during startup to raise the temperature of gases above the dew point. A 1.5 inch Aerotec cyclone, following the heater, was used to remove particulates during startup of the combustor, when water vapor condensing in the first two cyclones caused them to operate at reduced efficiency. Fine particulates were removed with a Pall Model MD-600 filter, located upstream of the back-pressure control valve. This filter had a mean pore size of 165 microns and an area of 0.73 sq. ft. Before being vented, the off-gas entered a chiller and knockout to remove moisture so that the water content of the gas could be determined. Alternatively, the gas could be sent directly to a second knockout at room temperature and vented. A small portion of the off-gases were diverted to a refrigerator which lowered the dew point of the gas to about 35°F before it was sent to the gas analysis equipment.

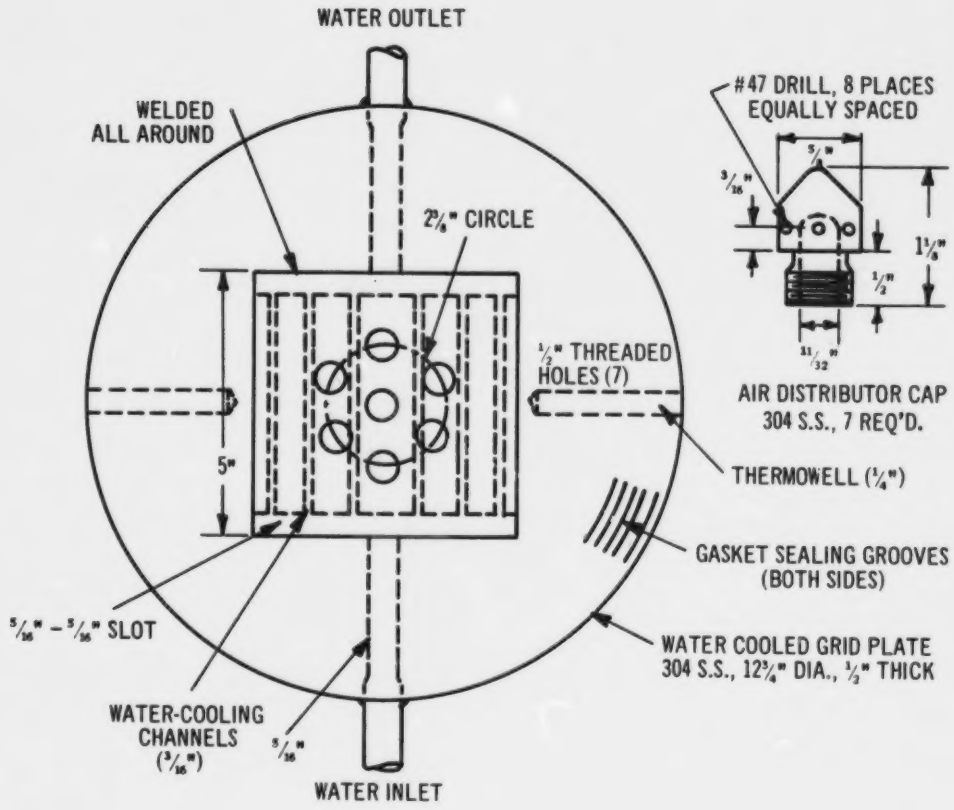


Figure 7. Combustor fluidizing grid

Gas analysis equipment included Beckman Model NDIR 315 analyzers for SO_2, NO, and CO, a Beckman Model 715 polarographic analyzer for O_2, and a LIRA Model 300 analyzer for CO_2. The concentration ranges of the analyzers used with the combustor are given below.

	Instrument No. 1	Instrument No. 2
SO_2	0-3000 ppm	
CO	0-1250 ppm	0-10 per cent
	0-6250 ppm	0-30 per cent
NO	0-500 ppm	
	0-1000 ppm	
	0-2500 ppm	
O_2	0-5 per cent	
	0-25 per cent	
CO_2	0-25 per cent	

Coal Feeder Test Unit

Figure 8 is a diagram of the apparatus used to test the Petrocarb coal feeder before use with the combustor. Air was used to pressurize the Petrocarb coal feeder and transport coal through the injection tube to the receiving vessel. The Petrocarb unit was equipped with pressure regulators for both the feed tank and injection air, a control valve for injection air, and a rotameter to indicate total air flow. The receiving vessel was mounted on a scale which indicated weight changes as small as 0.01 lb. Pressure in the receiving vessel was set at the desired value by means of a back pressure regulator. A differential pressure cell measured ΔP between the coal feed tank and receiving vessel. House air for the feeder first entered a bed of Drierite to reduce its moisture and thus keep the coal dry. Air leaving the receiving vessel was passed through a 65 μ filter to remove coal fines.

Experimental runs were first made at pressures of 70 psig and below in the feed tank. After some operating experience was obtained, modifications were made in the equipment to permit operation at pressures of 135 psig in the feed tank or about 10 atmospheres (absolute) in the receiving vessel. For operation at higher pressures, the Petrocarb unit was connected to an air compressor. Air from the compressor passed through two silica gel driers to keep moisture reaching the coal to a minimum. The original receiving vessel, rated for 100 psig, was replaced with one good for 250 psig. Heavy rubber hose was substituted for Polyflow tubing for runs made at higher pressures. Pressure regulators supplied with the Petrocarb feeder had a 125 psig limit and were replaced with regulators designed for higher pressures. Air from the compressor was stepped down in pressure with an additional regulator.

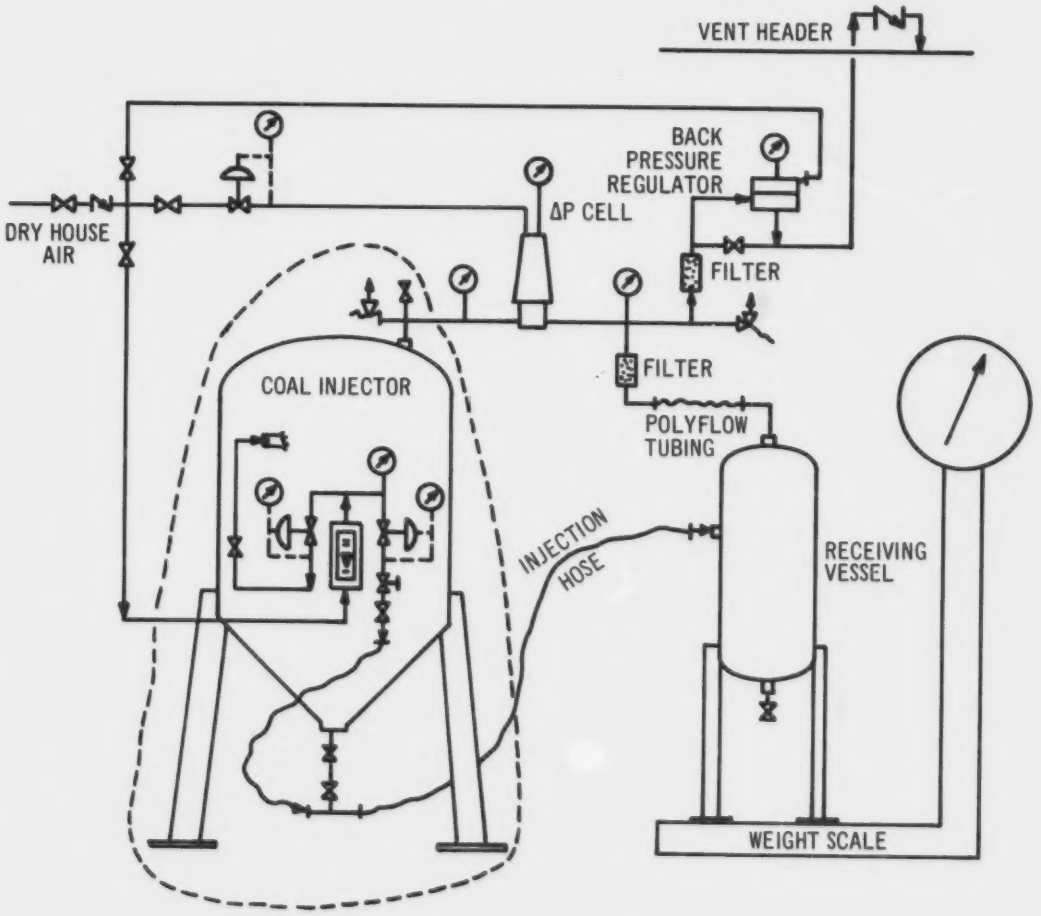


Figure 8. Coal feeder test unit (section within dashed lines provided by Petrocarb)

FLUIDIZED BED REGENERATION UNIT

Figure 9 is a schematic diagram of the Esso fluidized bed regeneration unit. The main components of this unit are (1) the burner, (2) the fluid bed regenerator, and (3) the gas handling and analytical equipment.

Burner

The burner, shown in Figure 10, was located at the bottom of the regenerator, under the fluidizing grid. It produced heat and a reducing gas mixture containing CO and H_2. The main parts were a tube to mix the fuel (propane + propylene) with air and a water-cooled grid to hold the flame.

The tubular part of the burner was made of 304 stainless pipe, 2 inches in diameter and 5.5 inches long. At the bottom of the tube were two baffles which supported a bed of 1/8 inch alumina beads and also helped to prevent channeling of the air-fuel mixture up the sides of the tube. Air and fuel entered at a tee below the burner tube; fuel entered the tee through a sparging tube containing eight-3/64 inch diameter holes at its tip to promote even distribution. The alumina beads further mixed the air-fuel mixture.

The burner grid was a 3 inch diameter x 1/4 inch thick brass plate which screwed onto the top of the burner tube. The grid was water-cooled and contained about 400-1/32 inch holes through which the air-fuel mixture flowed. On the underside of the grid was a disk of porous stainless steel which acted as a flame arrestor and prevented flashback into the burner tube.

The burner was ignited by a pilot light which was positioned near the side of the burner tube below the burner grid. The pilot light, in turn, was ignited by an electrode. This arrangement kept the ignition equipment away from the flame of the burner, where it would be damaged by excessive heat.

Batch Fluidized Bed Regenerator Vessel

Figure 11 shows the batch fluidized bed regenerator. The vessel was constructed from three sections of 12 inch carbon steel pipe and refractory lined with Grefco Litecast No. 7528. The interior of the regenerator was lined with a 3.25 inch diameter alumina tube. The height of the unit above the fluidizing grid was about 16 feet. A burner section, about 2 feet long, and lined with Bubbalite, was located under the grid. The burner was mounted on a flange which attached to the bottom of the burner section. Air and fuel required for regeneration entered the regenerator at the bottom of the burner. However, for some runs, a portion of the fuel and secondary air were added at various points above the fluidizing grid.

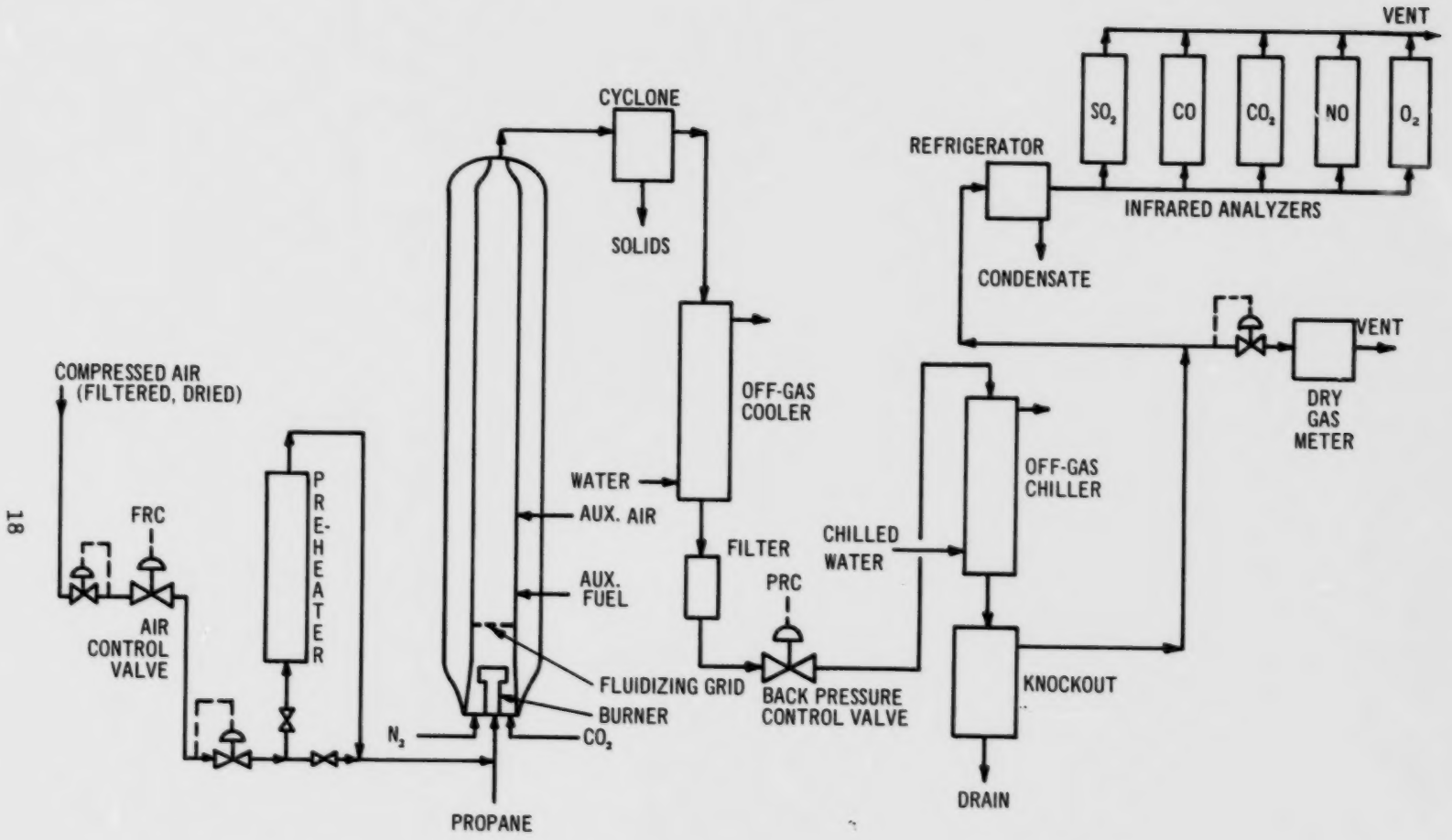


Figure 9. Fluidized bed regeneration unit

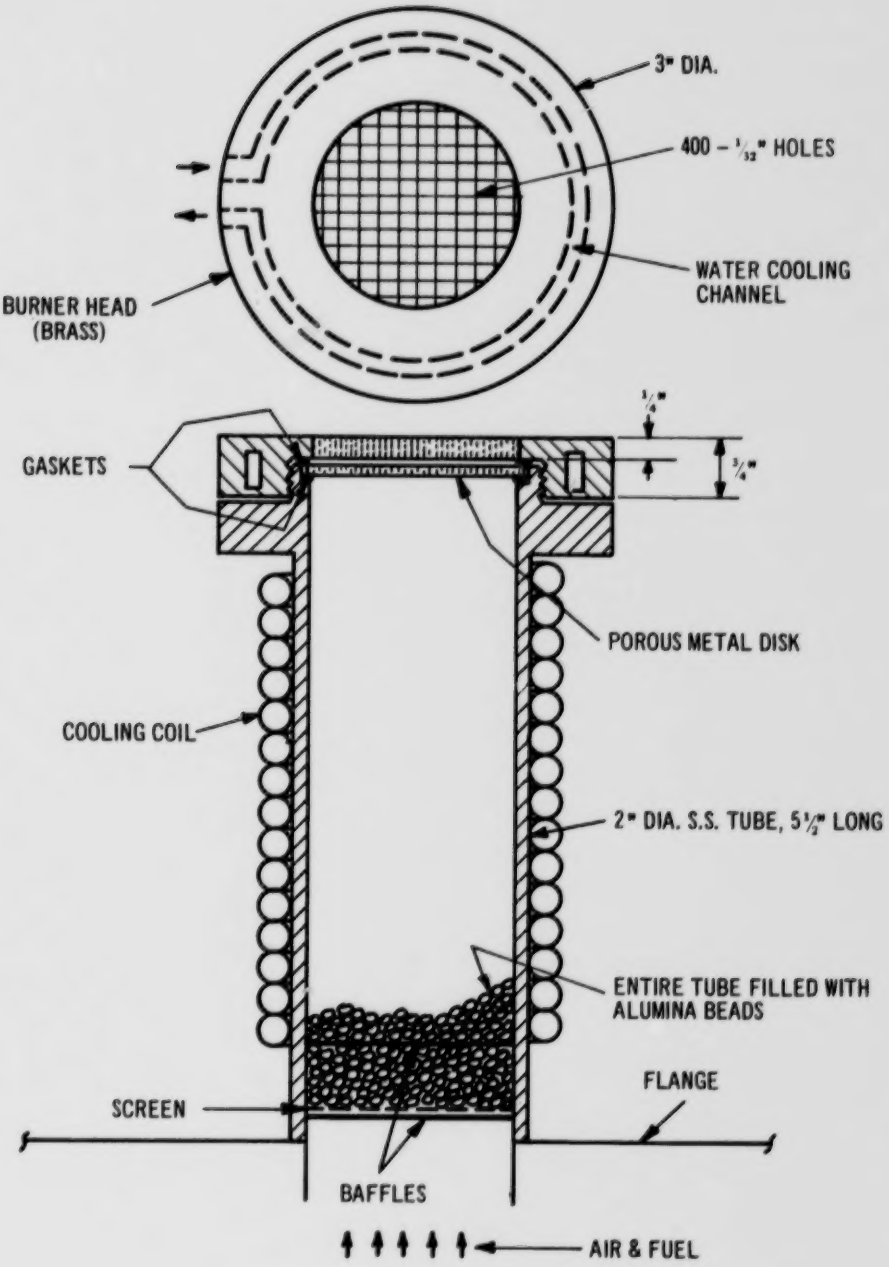


Figure 10. Regenerator burner

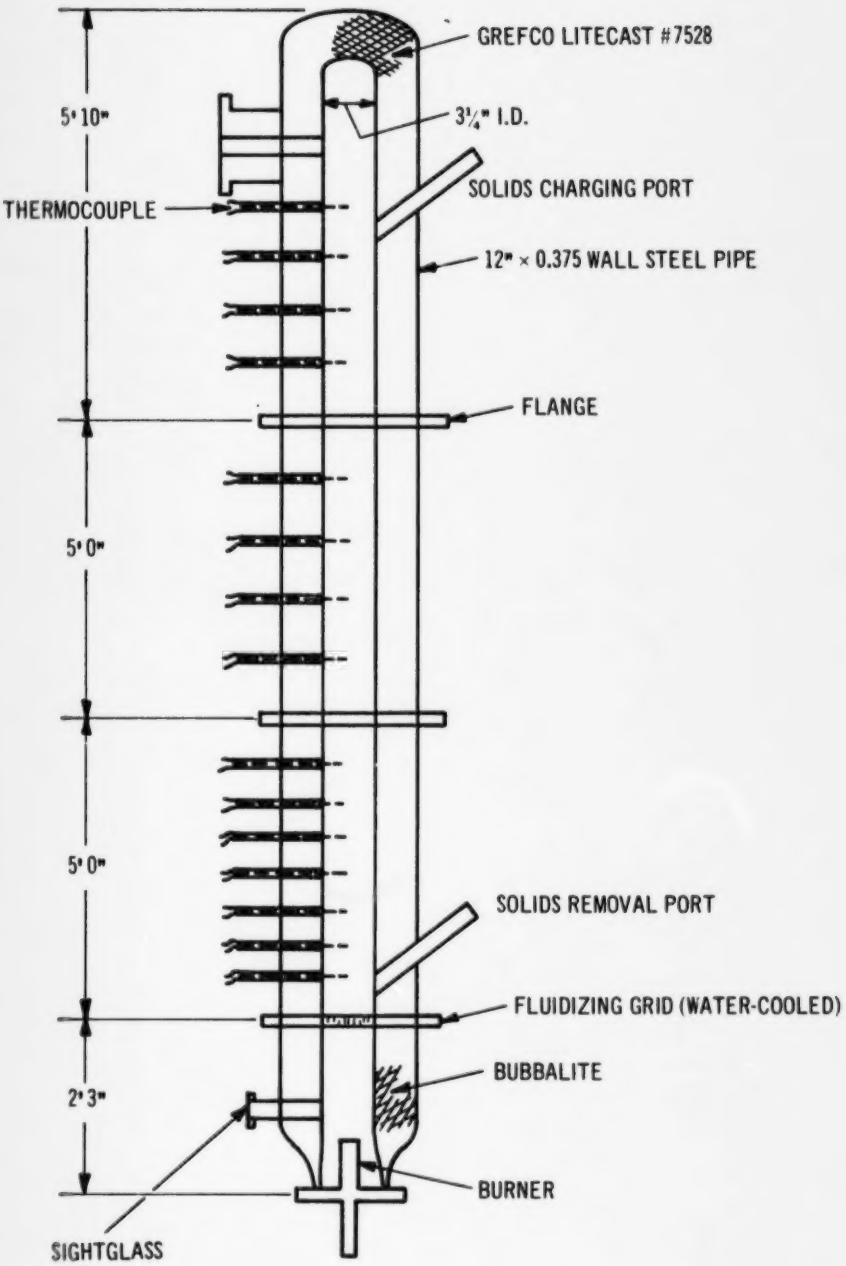


Figure 11. Fluidized bed regenerator

The maximum operating temperature and pressure of the batch regenerator were 2100°F and 10 atm., respectively. Thermocouples, spaced 6 inches apart, were used to judge bed temperature. Besides air and fuel, N_2 and CO_2 could be fed into the reactor. For runs in which secondary air was not added above the fluidizing grid, O_2 was added near the top of the regenerator to convert elemental sulfur, which might plug lines, to SO_2. All gas flows and system pressure were under automatic control.

Air could be preheated before entering the burner by using an electrical air preheater with 7.5 kilowatts capacity. Kanthal wire was wound around the outside of the ceramic tube in each of the two lower sections of the regenerator. Each heater had a capacity of 7.5 kilowatts and could be used to provide extra heat to the bed.

The fluidizing grid for the regenerator was made of 304 stainless steel and contained 69-5/64 inch holes for the passage of fluidizing gases. A five inch square at the center of the grid was water-cooled.

Solids were charged into the regenerator through a port located near the top of the unit. Solids could be removed through another port located just above the fluidizing grid.

Gas Handling and Analytical System

Gases leaving the regenerator were passed through a cyclone to remove entrained solids and then to an off-gas cooler which reduced temperature to the desired level. Downstream of the off-gas cooler, the regenerator shared equipment with the batch combustor. Thusly, the gas stream entered a solids filter, back pressure control valve, chiller and knockout before being vented. The analytical instruments, too, were shared with the combustor. However, an additional Beckman Model NDIR 315 analyzer was used to determine the concentration of SO_2 in the 0-15% range.

Air for the regenerator was supplied by a compressor. Other gases came from cylinders. Fuel cylinders (propane-propylene) had to be kept in a steam-heated hot-box at 120°F in order to maintain sufficient vapor pressure. In addition, fuel lines near the regenerator were heated to prevent fuel from liquefying. Figure 12 is a photograph of the fluidized combustor and regenerator. Figure 13 is a photograph of the control panel used to operate the units.

LABORATORY FIXED BED UNITS

Steel Reactor

A 1 inch O.D. stainless steel reactor (0.75 inch I.D.) was used for fixed bed studies examining reactions between NO and CO under simulated combustion conditions. The reactor was capable of operating at temperatures up to 1600°F at pressures up to 10 atm. Feed gases were purchased with various concentrations of NO, CO, CO_2, and O_2 in N_2 or A

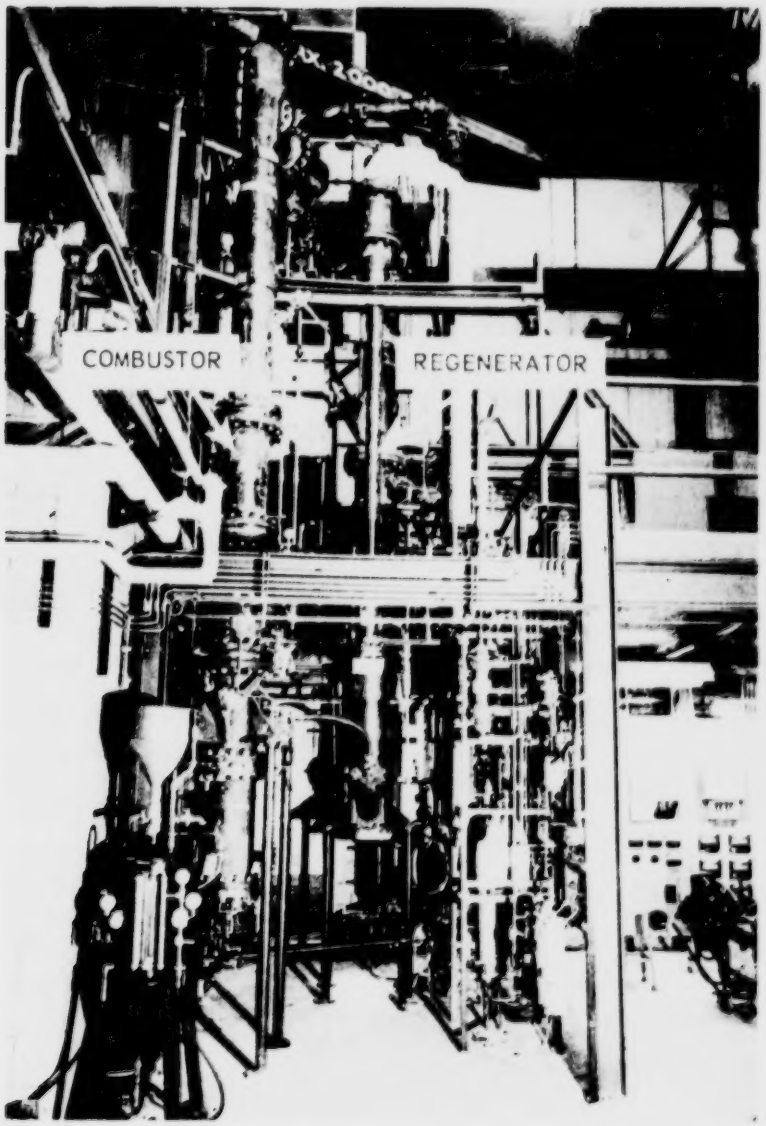


Figure 12. Fluidized bed combustion and regeneration units

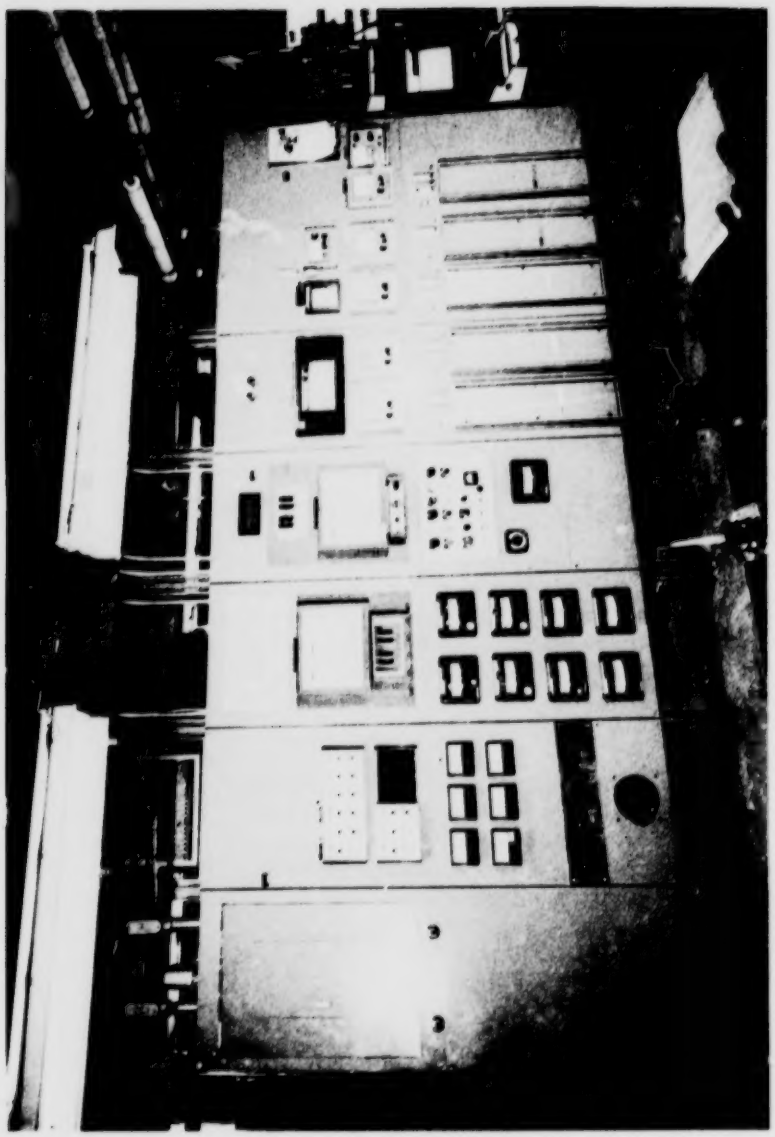


Figure 13. Fluidized bed unit control panel

diluent. Provisions were made to blend two gases before passing the gas mixture through the reactor. Rotameters were used to meter the gases. The reactor was packed with alumina beads which acted as a preheat section, followed by the bed material. The bed material was calcined limestone (1359) or dolomite (1337). The entire reactor was held in an electrically heated furnace. The off gases were analyzed for NO and CO by Beckman Model 315 NDIR analyzers. CO_2 was measured by an MSA Model 200 NDIR analyzer. The gases were cooled to 35°F before analysis to remove water. A Beckman Model 715 polarographic analyzer was used to measure O_2 concentrations in the product. The blended feed gas could also be diverted to the analyzers for measurement.

Ceramic Reactor

A one inch I.D. ceramic reactor was used to study regeneration of $CaSO_4$ at temperatures up to 2000°F and pressures up to 9.5 atm. The reactor consisted of a one inch I.D. ceramic tube mounted axially in a 3 inch Schedule 5 304 stainless steel pipe.

The reactor was heated electrically by resistance heater windings on the external surface of the ceramic tube. The overall length of the ceramic tube was 28 inches but only the mid 24 inch section was heated. For most of the runs, a 40 gm charge of $CaSO_4$ (anhydrite) or partially sulfated lime was used and was placed about 17 inches above the bottom of the ceramic tube. The lower section of the ceramic tube was filled with ceramic beads and served as a preheat section for the feed gases flowing up through the beads. Temperature was measured by a thermocouple inserted in a 1/4 inch O.D. ceramic well located axially in the center of the 1 inch reactor. A second thermocouple in this well operated the temperature controller.

The feed gas was produced by metering a CO/N_2 blend and a CO_2/N_2 blend to give the desired feed gas composition and flow rate. Rotameters were used for gas flow measurement. The product gas was then cooled, passed through a filter, back pressure regulator, and chiller before analysis for SO_2 content in a Beckman Model 315A infrared analyzer.

MATERIALS

Coal

The coal used in the batch fluidized bed combustor, and in the test program for the coal feeds, was a high volatile (A) bituminous coal from Consolidation Coal Company's Arkwright mine in West Virginia. It was ground to -30 mesh by Penn-Rillton Co. The specified particle size distribution is given in Table 1. A proximate and ultimate analysis was made on each of two samples of coal. Sample No. 1 was taken directly from the fifty pound bag in which it was supplied; sample No. 2 was taken from the receiving vessel used in the test program for the coal feeder, after it had been fed from the Petrocarb injector. The results of the analyses of both samples are given in Table 2.

TABLE 1. COAL PARTICLE SIZE DISTRIBUTION
Penn-Rillton Co. Grind B-2 Specification

U. S. mesh size	10	20	30	40	100	200	pan
Wt. fraction on screen	0	4.5	15.5	14	35.5	12.5	18

Limestone and Dolomites

A limestone and two dolomites were used in the experimental studies. The stones and their properties are given in Table 3. Various particle size ranges of these materials were used and are specified in the sections where the experimental results are described.

$CaSO_4$

A high purity form of anhydrous $CaSO_4$ was used in the regeneration studies. The material was purchased from W. A. Hammond Co. under the trade name "Drierite" in 10 x 20 mesh particle size range.

EXPERIMENTAL PROCEDURES

Cold Model Test Unit

The measurements of bed expansion ratios, quality of fluidization and minimum fluidization velocity were made visually.

The rate of solids transfer was evaluated by two methods. In one method solids transfer was permitted only from the prototype regenerator to the prototype combustor, and the increase in solids inventory in the combustor was measured over a timed interval. In the second method, transfer was accomplished in both directions, and a charge of painted

TABLE 2. COMPOSITION OF COAL USED IN ESSO BATCH-FLUIDIZED BED COMBUSTION PROGRAM

Source: Consolidation Coal Co. - Arkwright Mine

Proximate Analysis

Component	Wt. Percent Sample #1 (bag)	Sample #2 (receiving tank)
Moisture	1.00	1.03
Ash	8.11	8.01
Volatile matter	36.86	36.69
Fixed carbon	54.03	54.28

Ultimate Analysis

Component	Wt. Percent Sample #1 (bag)	Sample #2 (receiving tank)
Moisture	1.00	1.03
Ash	8.11	8.01
Total carbon	76.26	76.67
Hydrogen	5.30	5.30
Sulfur	2.66	2.49
Nitrogen	1.49	1.47
Chlorine	0.07	0.08
Oxygen (by difference)	5.11	4.95

Higher Heating Value, Btu/lb.

Sample No. 1	Sample No. 2
14,045	14,070

TABLE 3. PROPERTIES OF LIMESTONE AND DOLOMITES

Designation	Quarry source	Stone type	Chemical Analysis, Wt.% CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3
1359	Grove Lime Co. (Stephen City, Va.)	Limestone	97.0	1.2	1.1	0.3	0.2
1337	Chas. Pfizer Co. (Gibsonburg, O.)	Dolomite	54.0	44.0	0.9	0.2	0.3
Tymochtee	C. F. Duff & Sons (Huntsville, O.)	Dolomite	53.8	38.7	5.3	0.9	1.2

limestone was added just after the combustor transfer catch pocket to serve as a tracer. The time required for the painted limestone to reach the regenerator was measured, and knowing the volume of the transfer line, the transfer rate was calculated.

The stone used in the studies was a wide particle size distribution of calcined limestone (-6 to +20 U.S, mesh) representative of solids from the limestone grinding equipment.

Coal Feeder Test Unit

Before a run, the coal feeder was checked to see that it contained 50-100 lbs. of coal. The feeder and receiving vessel (see Figure 8) were then pressurized and the back pressure regulator located downstream of the receiving vessel was adjusted so that the pressure in the vessel was less than the pressure in the feeder by the desired amount (routinely 3 psi). Flow of injection air was started by setting the injection air pressure regulator to about ten psi above the feed tank pressure, opening the injection air shutoff valve, and adjusting the metering valve until the desired air flow was indicated on the rotameter. The vibrator, which was attached to the feeder directly above the mixing tee, was turned on. If necessary, the back pressure regulator on the receiving vessel was readjusted to bring the feed tank to receiver ΔP to the desired value. Coal feed was started by opening the coal feed valve. Weight of the receiving vessel was recorded, typically every minute, so that the coal feed rate could be determined.

To stop the flow of coal, the coal feed valve was shut. Injection air was left on for several minutes after the feed valve was closed so that the mixing tee and injection tube could empty. If injection air was stopped with coal remaining in the tee or injection tube, a plug usually formed when the feeder was restarted.

Fluidized Bed Coal Combustion Unit

Operation of the batch fluidized bed combustor can be divided into four phases: startup, ignition and pre-heating, coal feeding, and shutdown. Startup consisted of those activities preliminary to ignition of the propane burner. These activities included checking equipment to make sure it was ready for a run, checkout of the analyzer calibration, charging solids, turning on electrical circuits and the air compressor, turning on all cooling water systems (fluidizing grid, burner, coal probe, steam coils, condenser) and purge nitrogen systems (pressure taps, sight-glasses, d/p cells).

To ignite the propane burner, air and fuel flows were set and the ignition electrode was activated. Safety devices shut down all flows if ignition was not obtained within ten seconds or if a flame-out occurred afterwards. A safety interlock prevented startup for 3 minutes after an automatic shutdown to assure adequate purging of the combustor. Subsequent to ignition, air flow and combustor pressure

were adjusted to the values desired for making the run. All gas flows and pressure were controlled automatically.

Preparation of the coal feed system for a run consisted of setting the flow of injection air and activating and adjusting the coal feeder to combustor ΔP control system. Coal injection could be started only after the temperature in the combustor was high enough for self-ignition of the coal to occur. Propane flow to the burner was stopped automatically at the same time that feeding of coal was started. An automatic safety circuit would shut down coal injection if the combustor temperature dropped too low to ensure combustion of the coal or if the feeder to combustor ΔP dropped below a pre-set minimum (about one psi).

Data on the weight of the coal feeder vs. time was taken so that the feed rate of coal could be determined. Another method of estimating the feed rate was to observe the oxygen concentration in the off-gas from the combustor. A rapid rise in oxygen concentration was usually the quickest way of determining that a problem was developing with the coal feeding system.

Temperatures in the combustor could be adjusted by regulating the amount of water entering the three pairs of cooling coils. The feed rate of coal could be adjusted by changing the flow of injection air.

To shut down the combustor routinely, the coal feed valve was shut, fluidizing air was stopped, and a nitrogen purge was started to preserve the solids. Flow of injection air was kept on for several minutes so that the coal feed line could be cleared of coal. All water flows were reduced. Solids could be discharged from the reactor (by blowing them out of a port located just above the fluidizing grid) after the unit bed cooled overnight.

Fluidized Bed Regeneration Unit

Operation of the regenerator was similar to the combustor except that no coal feeding was involved. Preliminary startup of the unit included checkout of the calibration of the analytical instruments, activation of electrical systems and air compressor, check of the propane system, and turning on all cooling water systems.

The empty regenerator was first preheated to minimize condensation of water after solids were added. The burner was then shut off and solids were charged through a port located near the top of the unit. Reheating of the bed was then begun and pressure and air flow were adjusted to meet the conditions selected for the run. If desired, air could be electrically preheated. When the bed was near the temperature of the run, reducing conditions were established by increasing the flow of fuel. Additional fuel could be added through the burner or, alternatively, directly into the bed. Auxiliary air could also be added, higher in the bed, to reduce formation of CaS. When auxiliary air was not used, it was necessary to provide a small stream of O_2 near the top of the regenerator to oxidize any sulfur which formed and which might otherwise plug lines.

Shut down was accomplished by stopping the flow of fuel and air and reducing the pressure in the system to atmospheric. A nitrogen purge was applied to prevent combustion of any carbon deposits in the reactor and to prevent moisture from reaching the solids until they had cooled sufficiently to be removed (overnight).

Laboratory Fixed Bed Units

Steel Reactor -

The reactor was packed with 40 gm of calcined limestone or dolomite and inert alundum beads. The bed was heated to the operating temperature in the presence of N_2. The proper blend of inlet gases was then made, analyzed in the continuous IR analyzers and then admitted downflow into the reactor. The outlet gases were continuously analyzed.

Ceramic Reactor -

The lower section of the reactor was first packed with Alundum beads to serve as the preheat section. For most runs, 40 gm of bed material was then placed above the preheat section. In some runs, the bed charge was increased to 60 gm. After heating to the proper temperature in the presence of a stream of N_2 passing upflow through the bed, the feed gases were blended to give the proper composition and then admitted upflow into the reactor. The product gases were analyzed continuously. Since this unit was used to study regeneration of sulfated material, the primary component in the product gas was SO_2 formed by the reduction of the sulfated bed material. The SO_2 concentration in the product gas decreased as the bed material was reduced, and the runs were terminated when the SO_2 concentration decreased to a very low level. The time of the runs ranged from 1 to 2 hours, during which time five to ten times the stoichiometric amount of reducing gas was passed over the bed. After the bed cooled, the charge was removed, weighed and analyzed for total sulfur content.

SECTION V

DEVELOPMENT OF EXPERIMENTAL EQUIPMENT AND PROCEDURES

COAL FEEDER

Introduction

The coal feeding system for the pressurized batch-fluidized bed combustor must be capable of metering 6-28 lbs./hr. of powdered coal (-30 mesh) into the combustor against pressures of up to 10 atmospheres. A Petrocarb ABC injector, which is a small version of the solids feeder to be used with the combustor of the Miniplant, was chosen to feed coal into the batch combustor. An experimental program was undertaken to test the suitability of the Petrocarb feeder for doing this. The purpose of the program was to determine what modifications of the Petrocarb system were needed to make it operate satisfactorily and to gain experience in feeding coal prior to startup of the combustor.

Argonne National Laboratory had tested the suitability of the Petrocarb ABC injector for feeding 20-40 lbs./hr. of coal, limestone, and mixtures of coal and limestone, into a bench scale combustor-regenerator (1). Coal feed rates averaged 31.6-45.7 lbs./hr. for runs at atmospheric pressure to 97.8-179.3 lbs./hr. for runs with 75-82 psig pressure in the receiving vessel. Many runs were characterized by feed rates that fluctuated widely. Argonne terminated work with the Petrocarb feeder when they concluded that it could not feed coal at steady rates in the flow ranges they required. Argonne made only minor modifications to the system supplied by Petrocarb. At Esso, it was hoped that the Petrocarb system could be made to perform satisfactorily if additional modifications were made.

Theory of Operation

Operation of the Petrocarb solids feeder depends on gravity flow of solids through an orifice and subsequent pneumatic conveying of the solids to the receiving vessel. These two operations have been studied by others with many different types of solids (2). For example, it is known that the reduction in "viscosity" of a bed of powder will result in an increased flowrate through an orifice. This reduction in viscosity can be accomplished by pressurizing the bin by means of a connection atop a closed vessel or by adding an aeration bleed at the base of an open bin. Either procedure results in a small stream of gas leaving with the solids through the orifice. This additional stream of gas "lubricates" the flow at the orifice and reduces the viscosity at this point. By means of this principle, solids can

be made to flow through smaller openings than would be possible by simple gravity flow. Increasing the pressure, as can be done in the Petrocarb solids feeder, increases the lubricating effect at the orifice and permits solids to flow at a greater rate.

Solids flow through the orifice at the bottom of the Petrocarb feeder and enter a mixing tee where a moving stream of air picks up and conveys the solids through a tube to the receiving vessel. The relationship between pressure drop per unit length of tube and superficial velocity is similar to that obtained for a tube with gas only flowing. However, pressure drop is higher due to the force required to maintain the solids in suspension and move them along with the gas stream. At constant superficial velocity, pressure drop increases with increasing solids loading. In order to maintain a given feed rate of solids through the tube, the superficial gas velocity must not fall below a certain critical value, called the saltation velocity. Below the saltation velocity, which is a function of solids flow rate for any particular gas-solid system, particles settle out in the tube.

It is interesting to compare the saltation velocity for horizontal transport with the minimum velocity required to transport solids vertically, called the choking velocity. Experimental data indicates that saltation velocities and choking velocities are identical for uniform sized particles. However, for mixed size material saltation velocities are three to six times as great as choking velocities. This is in accord with numerous qualitative statements appearing in the literature on pneumatic transport to the effect that the velocity required to convey materials horizontally is several times as great as that required to convey vertically.

Experimental Results

Work with the Petrocarb solids feeder was divided into two sections. The purpose of the initial work was to modify the feeder so that it could deliver coal smoothly and dependably at the required rates. The modified equipment would be used to collect data on feed rate of coal vs. feed tank pressure, feed tank-receiving vessel pressure differential, and injection air flow rate. Table 4 gives results of 68 runs made with the modified Petrocarb Model 16-1 ABC injector. A 3/16 inch orifice was used for all runs except no. 22, in which a 7/32 inch orifice was used. After run no. 22, the taper of the original 3/16 inch orifice was made steeper (see Figure 14).

Modification of Petrocarb Feeder

The Petrocarb ABC injector was designed for much higher solids feed rates than 6-28 lbs./hr., which is required for use with the combustor. Therefore, modification of the unit to permit lower feed rates was

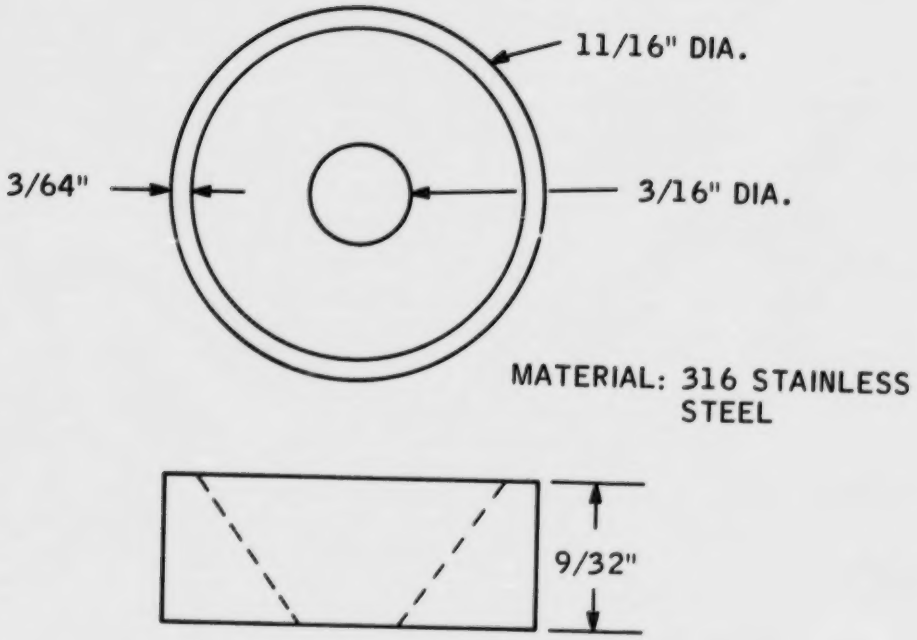


Figure 14. Coal feeder orifice

Table 4. COAL FEED RATES WITH A MODIFIED PETROCARB MODEL 16-1 ABC INJECTOR
Orifice size = 3/16 inch
Coal = -30 mesh

Run No.	Injection Hose	Feed tank pressure, psig	Receiving vessel pressure, psig	Air flow rate, SCFM	Average coal feed rate, lb/hr.	Comments
1	1/4 in. x 25 ft. Polyflow	5	0	1.0	1.0	Injection hose wrapped around receiver. Plugged after 15 min.
2		20	0	2.0	7.8	Injection hose plugged after 35 min.
3	1/2 in. x 25 ft. Rubber (Petrocarb supplied)	5	0	1.0	10-44	Hose wrapped around receiver. Erratic flow. Plugged after 13 min.
4		5	0	1.0	20	
5		5	0	1.6	6.5	Hose in 30 inch loops on floor. Ran well.
6		10	0	2.3	45	
7		20	0	2.3	125	
8		5	0	2.3	7.6	Conditions of Run No. 5 repeated.
9	1/4 in. x 25 ft. Polyflow	20	0	2.3	8.0	Hose in 30 inch loop on floor. Flow stopped after 19 min.
10		20	0	2.3	21	Flow stopped after 9 min. High static charge on injection hose.
11		20	0	2.6	17	Flow stopped after 10 min.
12	1/4 in. x 15 ft. copper	10	0	2.3	12.3	Injection hose in one large loop on floor.
13		5	0	1.6 1.0	7.3 28	Coal flow increased when injection air decreased.

Table 4 (continued). COAL FEED RATES WITH A MODIFIED PETROCARB MODEL 16-1 ABC INJECTOR

Run No.	Injection Hose	Feed tank pressure, psig	Receiving vessel pressure, psig	Air flow rate, SCFM	Averaged coal feed rate, lb/hr.	Comments
14	1/4 in. x 15 ft. copper	20	16	1.6	18.0	
15		40	36	2.0	21.1	Vibrator used.
16		60	56	2.0	24.0	Vibrator used.
17		40	38	2.0 1.3 1.0 0.7	7.2 22.3 25.1 34	Coal flow increased as injection air decreased. Vibrator used.
18	1/4 in. x 15 ft. copper	40	36	2.0	12.8	
19		70	67	2.0/1.3	16.8/37.0	Ran only 10 minutes.
20		70	67	1.3	32.0	
21		60	57	1.3	26.6	
22	1/4 in. x 15 ft. stainless steel	70	67	2.0	20.2	7/32 inch orifice used for this run.
23		70	67	1.3	28.7	Taper of orifice made steeper.
24		70	67	2.0	18.6	
25		60	57	2.0	16.5	
26		40	37	1.3	19.8	
27		40	37	2.0	8.2	
28		70	67	2.6	9.8	
29		70	67	1.6/1.3	24/31.6	Higher coal rate ran only 3 min.

Table 4 (continued). COAL FEED RATES WITH A MODIFIED PETROCARB MODEL 16-1 ABC INJECTOR

Run No.	Injection Hose	Feed tank pressure, psig	Receiving vessel pressure, psig	Air flow rate, SCFM	Average coal feed rate, lb/hr.	Comments
30	1/4 in. x 15 ft. stainless steel	70	67	2.6	8.3	
31		70	67	2.6	13.8	Bored out tee-injection tube connector.
32		40	37	2.0	5.8	
33		60	57	2.0	15.4	
34		60	57	1.3	30.6	
35		40	37	1.3	21.9	
36		60	57	2.3	8.0	
37		70	67	2.0	24.3	
38		20	17	1.3	10.1	
39		20	17	0.65	29.9	
40		60	57	1.6	28.8	
41		40	37	1.0	35.4	Frequent plugging
42		40	37	1.6	16.3	
43		70	67	2.3	15.8	New Syntron vibrator installed.
44		70	67	1.6	25.9	
45		70	67	1.3	40.9	
46		60	67	1.6	28.6	
47		70	67	1.6	29.1	
48		60	57	1.3	34.6	

Table 4 (continued). COAL FEED RATES WITH A MODIFIED PETROCARB MODEL 16-1 ABC INJECTOR

Run No.	Injection Hose	Feed tank pressure, psig	Receiving vessel pressure, psig	Air flow rate, SCFM	Average coal feed rate, lb/hr.	Comments
49	1/4 in. x 15 ft. stainless steel	121	118	2.6	27.5	Pressure at rotameter = 155 psig
50		135	132	3.5	15.7	
51		135	132	4.0	6.1	
52		135	132	3.1	25.6	
53		106	103	2.6	19.4	
54		106	103	2.6	26.3	Adjusted calibration of DP cell-was off slightly for runs 49-53.
55		135	132	3.5	12.6	
56		121	118	3.1	17.7	
57		106	103	3.1	17.1	
58		91	88	2.2	24.9	Cleaned filter before run.
59		121	118	3.1	17.4	
60		135	132	3.1	23.0	
61		135	132	4.0	6.9	
62		121	118	2.6	26.1	
63		121	118	3.5	9.7	
64		106	103	3.5	4.4	
65		106	103	3.1	8.8-12.7, avg. 9.9	Problems with air flow.

Table 4 (continued). COAL FEED RATES WITH A MODIFIED PETROCARB MODEL 16-1 ABC INJECTOR

Run No.	Injection Hose	Feed tank pressure, psig	Receiving vessel pressure, psig	Air flow rate, SCFM	Average coal feed rate, lb/hr.	Comments
66	1/4 in. x 15 ft. stainless steel	91	88	2.6	15.4	Minor problems with air flow.
67		135	132	3.7	11.3	Minor problems with air flow.
68		135	132	3.3	20.9	Minor problems with air flow.

necessary. Factors which affect feed rate are size of the orifice (5/16 inch supplied) and size of the tube connecting the feed tank with the receiving vessel (1/2 inch dia. x 25 feet hose supplied). An important part of the experimental program was to find that combination of orifice and injection hose size which would permit satisfactory operation over the range of required flowrates.

The first task was to establish a satisfactory size for the orifice. Orifice sizes of 1/8 inch, 5/32 inch, 3/16 inch, and 7/32 inch were tried but, with the two smaller orifices, coal would either not flow at all or flow intermittently upon tapping the orifice assembly. The two larger orifices plugged occasionally, but the 7/32 inch size produced coal feed rates which were too high. Thus, 3/16 inch was the optimum size to be used with the coal on hand (-30 mesh). After run no. 22, the taper of the orifice was made steeper. This reduced plugging.

Several injection tubes were tested. The first was a 3/16 inch x 25 feet copper tube (I.D. = 0.1275 inch) which was coiled around the receiving vessel so that the diameter of each coil was about 18 inches. The tube plugged frequently, and it was difficult to remove the plugs as this required disconnecting the tube, straightening it, and tapping an end to remove the plug. Polyflow tubing of 1/4 inch x 25 feet size (I.D. = 0.17 inches) was subsequently tried and had the advantage that it was translucent, so that plugs could be easily spotted, and that it could be readily put into any desired shape. When this tubing was wrapped around the receiving vessel, plugging usually occurred after only a few minutes. However, when placed in large (30 inch) loops on the floor, plugging occurred much less frequently. A 12 foot length of Polyflow tubing was also tested and gave considerably higher coal feed rates than did a 25 foot length. Use of Polyflow tubing was terminated because a static charge developed on the tubing during operation, which contributed to plugging.

A copper tube, 1/4 inch x 15 feet (0.19 inch I.D.), formed into one large loop was tried next. Decreasing the tube length made it easier to make a single loop and less plugging occurred than in longer tubes.

After run No. 14, a vibrator was attached to the mixing assembly at the bottom of the feed tank. The vibrator caused both the mixing assembly and the entire injection tube to vibrate and reduced plugging at both the orifice and injection tube. Plugging had continued to be a problem with the 1/4 inch x 15 feet (I.D. = 0.19 inch) copper tube, and it was replaced with a 1/4 inch x 15 feet (I.D. = 0.18 inch) tube of stainless steel. The stainless steel tube proved to be a significant improvement over the copper since it plugged less frequently. The improvement is probably due to the smoother surface of the stainless tube, which, reduces the tendency of the coal to stick.

Plugging of the injection tube is a serious problem because to remove

the plug it is usually necessary to disconnect the injection tube; hence, plugging of the tube during a run with the combustor would make shutdown of the combustor necessary. Plugging of the orifice in the mixing assembly is less serious as tapping in the area of the orifice usually removes the plug and coal flow resumes.

An additional modification made in the equipment was to bore out the inside of the tube fitting which connects the 1/2 inch diameter mixing tee located at the bottom of the feeder to the 1/4 inch diameter injection tube. The abrupt reduction in diameter had caused coal to accumulate in the tee and eventually plug. By boring out the connector, so that a gradual transition was made from 1/2 inch to 1/4 inch diameter, the plugging problem was eliminated. This change caused also a moderate increase in coal flow.

Calibration of Modified Feeder

A program was undertaken to determine how feed tank pressure, feed tank-receiving vessel pressure differential, and air flow rate affect the feed rate of coal in the modified Petrocarb injector. Data collected would make it possible to pre-set operating conditions needed to produce the desired coal feed rate.

For a given orifice, coal feed rate appears to be a function of pressure drop across the orifice of the coal feeder and the pressure in the feeder. The size of the injection tube and the injection air flow affect coal flow indirectly by causing more or less of the total pressure drop from feeder to receiving vessel to occur across the orifice rather than through the tube.

Figure 15 shows the effect of air flow rate on coal feed rate for four pressures of up to 70 psig in the coal feed tank. All data shown are for a 3/16 inch orifice, 0.18 inch I.D. x 15 feet long stainless steel injection tube, and a feed tank to receiving vessel pressure differential of 3 psig. Increasing the air flow rate through the injection tube causes a higher pressure drop across the injection tube and a correspondingly lower pressure drop across the orifice. Hence, coal flow decreases with increasing air flow.

It should be noted that not all of the air which passes through the air rotometer enters the injection tube. A fraction of the total air flow enters the feed tank to compensate for the small flow of air leaving the feed tank with coal through the orifice. Thus, the actual air flow in the injection tube is slightly less than that indicated by the air rotometer setting.

Figure 16 shows the effect of feed tank pressure on coal flow rate at constant air flow rate and feed tank to receiver ΔP. An increase in feed tank pressure permits coal to flow more readily through the orifice.

Figure 15

Effect of injection air flow rate on coal feed rate - low pressure

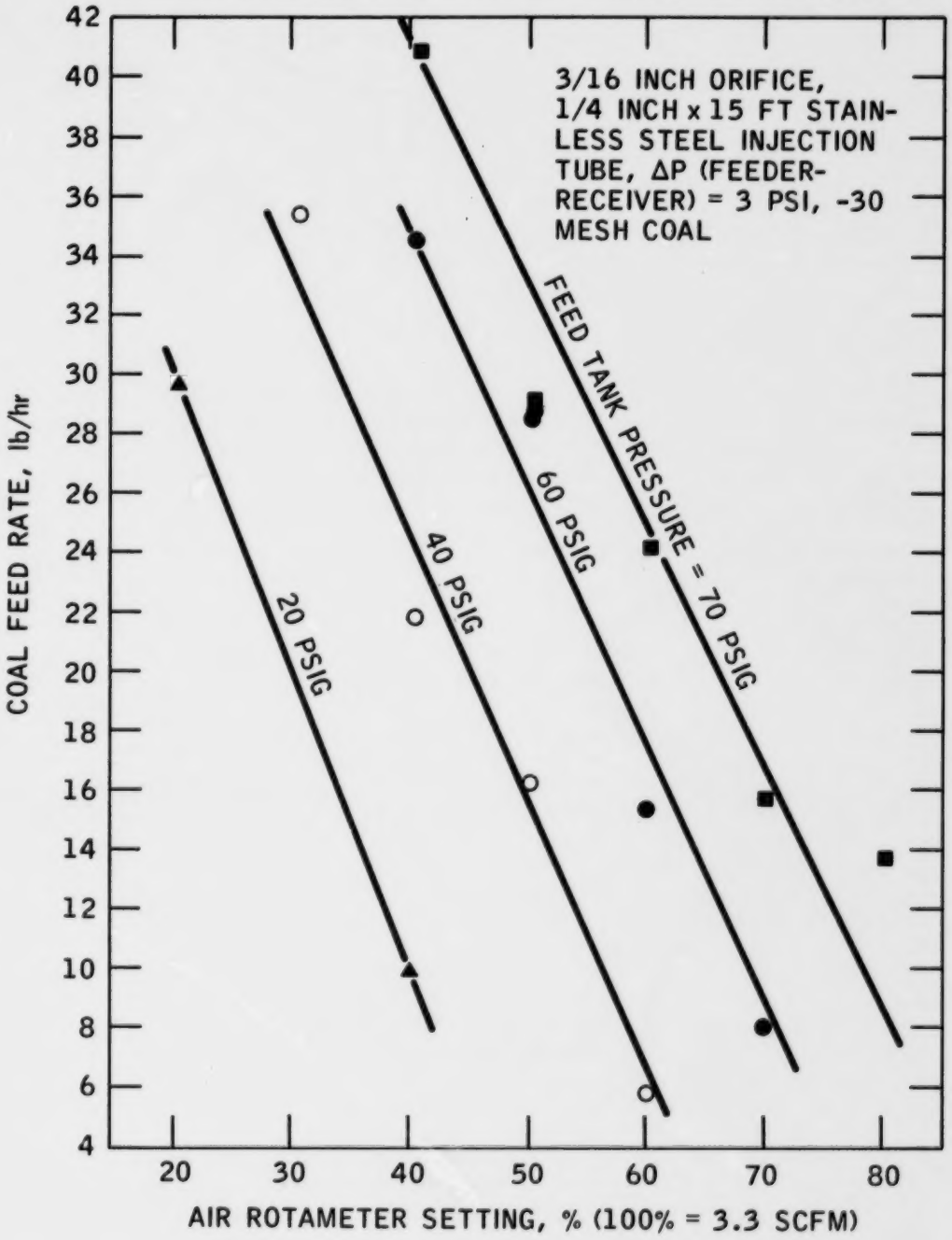


Figure 16

Effect of feed tank pressure on coal feed rate

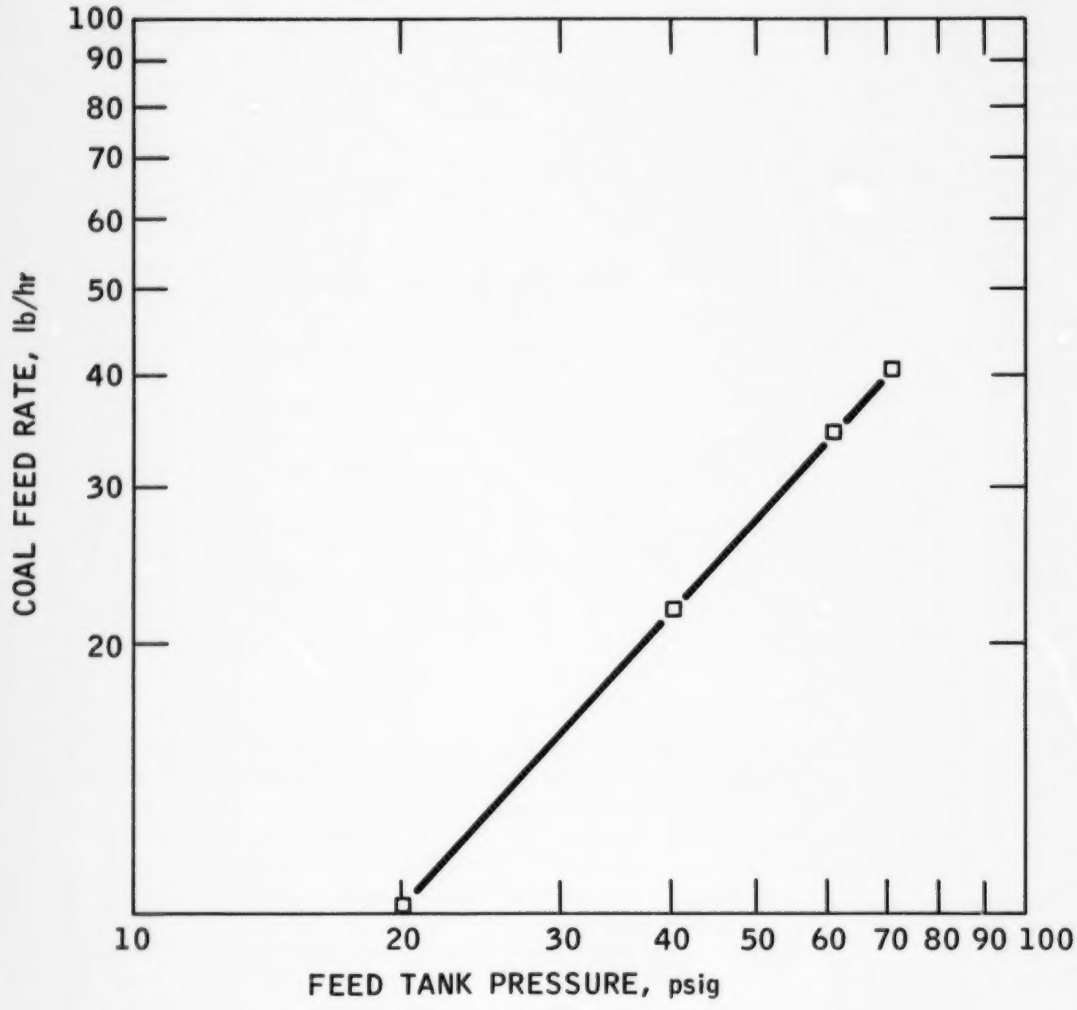


Figure 17 shows the effect of air flow rate on coal feed rate at four levels of feed tank pressure from 91 to 135 psig. At any given pressure, small changes in air flow rate change the coal feed rate considerably. The effect is similar to that shown in Figure 15 for data at lower pressures.

Figure 18 shows the effect of feed tank pressure on coal feed rates for three different air flow rates.

Plugging at the orifice and in the injection tube occurred much less frequently in runs made at higher pressures (above 90 psig) in the coal feed tank than at lower pressures. For example, during runs 49-64 (See Table 4) the injection line plugged only twice. The orifice plugged during one run, but the vibrator was not turned on at the time. These runs represent a combined total of about eight hours of operation. The flow of coal was also steadier at higher pressures.

A regression analysis was made on the data of runs 49-68 with receiver pressure and rotameter setting as the independent variables. The least squares correlation is

$$F = 36.0 + 0.371P - 0.873R$$

where F = coal feed rate, lb./hr.

P = pressure in receiving vessel, psig

R = air rotameter reading, % of scale

This correlation is valid only over the range of P and R in the experimental work (runs 49-68). These limits are 88-132 psig and 50-90%, respectively. The least squares lines are shown as the solid lines of Figures 17 and 18. Details of statistical tests of the model are given in Table 5.

BURNER

The burner for the batch fluidized bed regenerator had to handle a wide range of flowrates, up to a maximum of about 30 SCFM air and 1.5 SCFM fuel (60% propane + 40% propylene), in proportions ranging from strongly oxidizing to strongly reducing. Furthermore, it had to operate at pressures of 1-10 atm. and accept preheated air at temperatures up to about 800°F. As pressure, temperature, and fuel/air ratio increase, the tendency of a flame to flash back from the supporting grid into the burner tube also increases. These factors, combined with the need to produce a burner with a reasonably long service life, made the development of the burner a formidable task.

All burners that were designed and tested consisted of two main

Figure 17

Effect of air flow rate on coal feed rate - high pressure

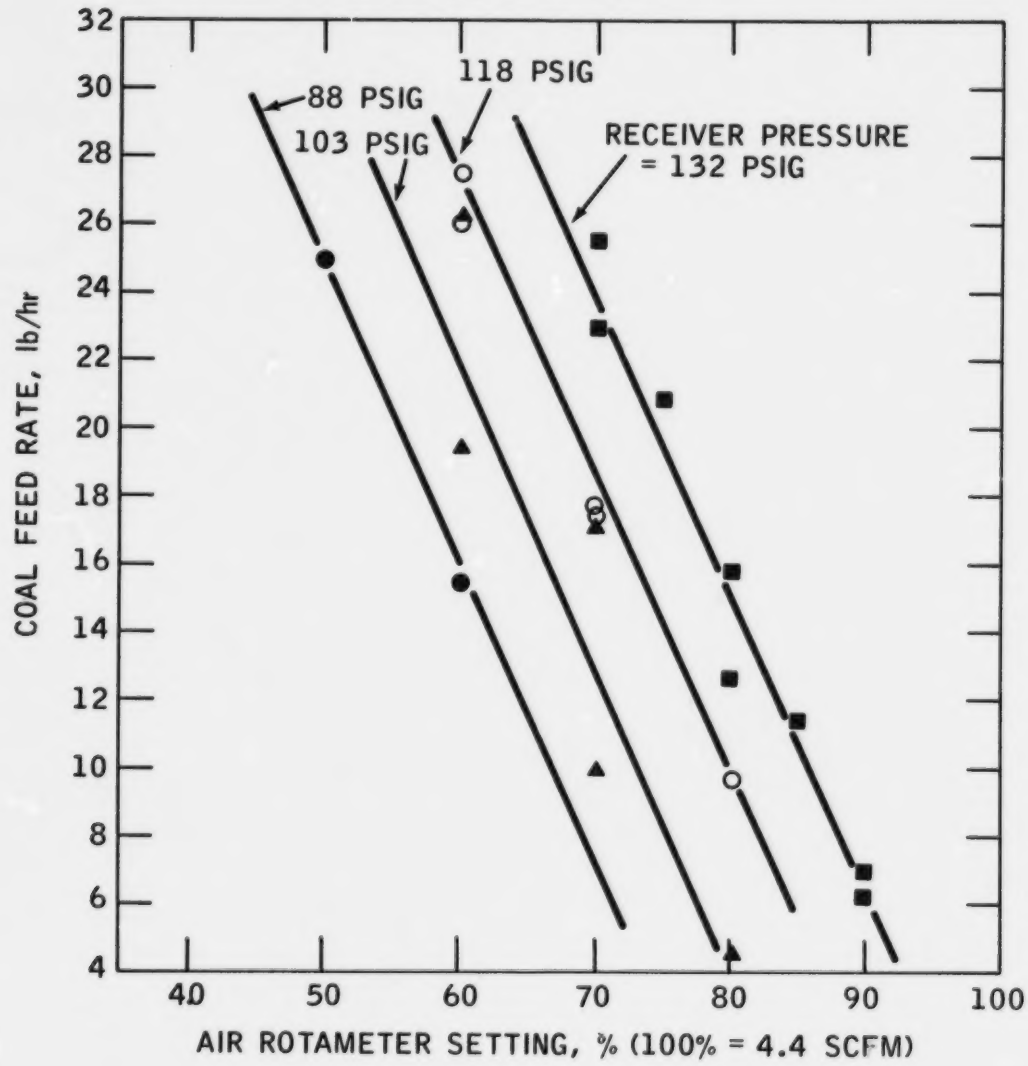


Figure 18

Effect of feed tank pressure on coal feed rate

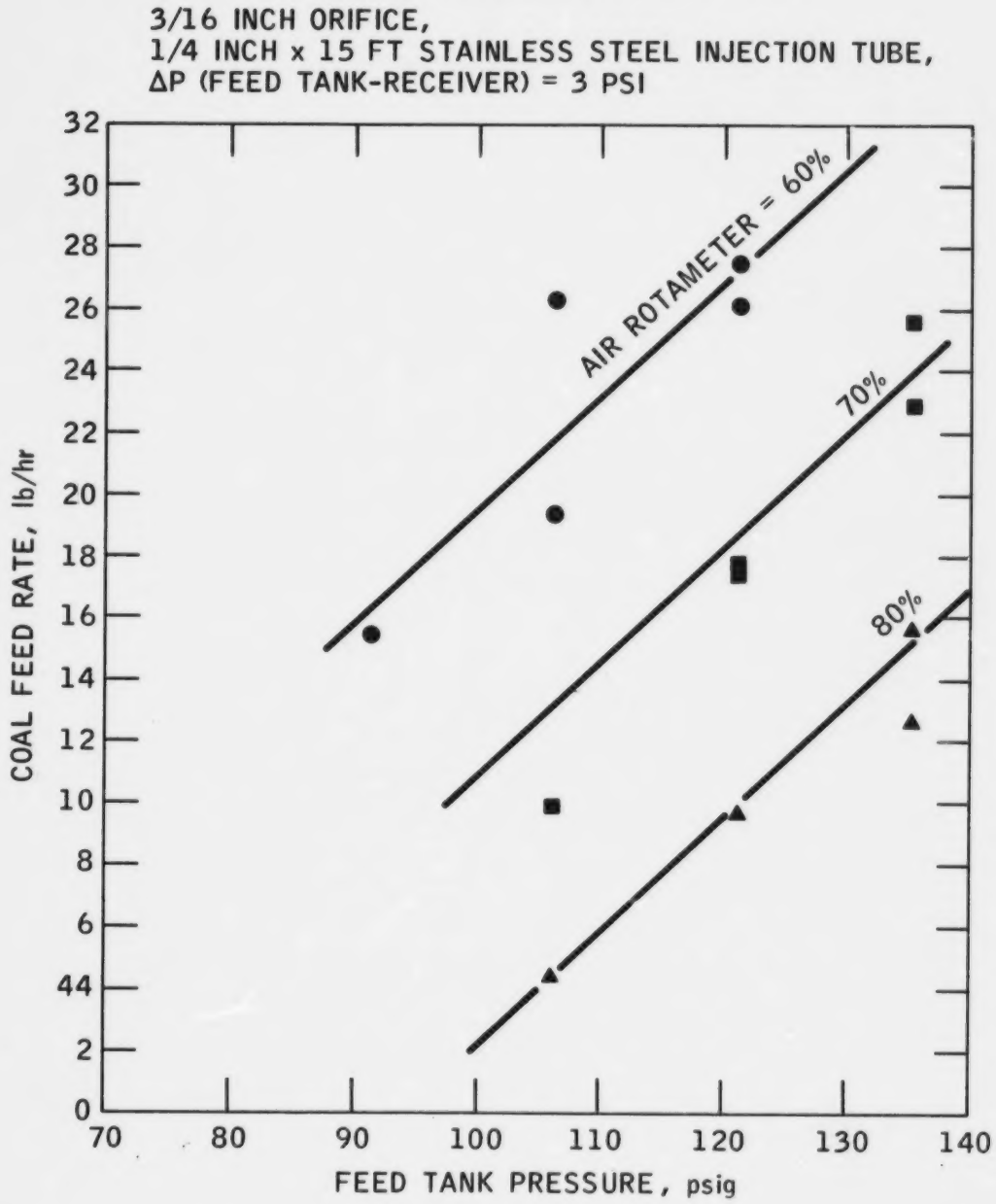


Table 5. RESULTS OF REGRESSION ANALYSIS OF COAL FEED TEST DATA

Dependent variables = F (coal feed rate, lb./hr.)
Independent variables = P (receiver pressure, psig)
R (rotameter reading, %)

Correlation Matrix

	P	R	F
P	1.000		
R	0.687	1.000	
F	-0.126	-0.781	1.000

Standard error of estimate = 2.033
F ratio for regression = 114.1
Fraction of explained variance = 0.931
Determination of correlation matrix = 0.528
Residual degrees of freedom = 17

Variable	Coefficient	Std. error of coeff.	T-ratio	F-ratio	Co-variance ratio
Constant	36.0				
P	0.371	0.042	8.86	78.46	0.47
R	-0.873	0.058	14.98	224.3	0.47

parts: the burner tube and the grid. (See Figure 10). The burner tube was essentially the same in all designs; it was a stainless steel tube about 6 inches long with a diameter of 2 inches. The burner tube was welded to a flange which attached to the bottom of the burner section of the regenerator. The burner tube contained baffles and was filled with 1/8 inch alumina beads to adequately mix fuel and air, which entered under the flange. Fuel entered through a sparging tube which distributed the fuel radially into the surrounding air. The position of the sparging tube in the burner tube could be adjusted to achieve optimum mixing. The best mixing occurred when the openings of the sparging tube were positioned at the tee where the air and fuel lines joined. It was also found that the number of baffles in the burner tube could be reduced from nine to two without any noticeable change in the appearance of the flame.

The first burner grid tested was a 1/8 inch thick plate of micrometallic mesh, which was welded to the top of the burner tube. Directly under the grid was a water cooling channel in the shape of a circle with four spokes. "Thermon" cement was placed between the mesh and the cooling tubes to promote good thermal contact. This burner assembly performed well in terms of its range of applicability for burning very lean to very rich. The reliability and durability of these grids was a problem, however. Three grids had been tried; the first and third lasted for only one to two runs while the second lasted considerably longer. Typically, cracks would develop in the mesh or around the weld. Variability in the service life of different grids was attributed to slight differences in construction.

In order to learn more about the cause of the loss of burner grids, the fine micrometallic mesh was replaced with coarser "Rigimesh". However, the Rigimesh grid, which caused a considerably lower pressure drop, burned out after only a few hours of operation.

Since no clear indication was then available on how to design a burner with a reasonable life expectancy, a new burner assembly was built to allow easy replacement of burner grids. This new burner had a grid which, rather than being welded, was attached to the top of the tube with a single bolt. This burner has been used successfully with the combustor for some time, perhaps because it has been used only for oxidizing flames.

A new burner grid for the regenerator burner was designed and built. It was a water cooled stainless steel plate containing 48-1/16" holes. The grid worked well at 10 atm with an oxidizing flame, but a flashback occurred with a reducing flame.

Another water cooled burner grid was built, this time of brass, to take advantage of the high thermal conductivity of this material. To help prevent flashback, the grid had small holes (400-1/32 inch), and a layer of micrometallic mesh was placed under the grid to act

as a flame arrester. This sandwich was held onto the burner tube by eight small studs. The burner performed very well for two runs (115R, 116R) but a flashback occurred during preparations for an additional run. The brass grid was not damaged but the baffles in the tubular section of the burner were destroyed. The probable cause of the flashback was a failure of the gasket sealing the metallic mesh flame arrester to the burner tube.

The design was modified to provide a more positive seal of the mesh to the burner tube. The mesh was welded onto the top of the burner tube and the brass grid was placed over the mesh and attached with studs. A gasket was still needed under the brass grid but, since it was directly under the cooling channel of the grid, it was kept cool. This design eliminated the second gasket, which would be exposed to higher temperatures. A radiation shield for the tubular section of the burner, made out of copper tubing (water-cooled), was also added to preclude the possibility of exceeding the self-ignition temperature of the fuel-air mixture before it reached the grid. The modified burner worked very well except for the breakage of a stud on two occasions. Disassembly and inspection of the burner after a series of seven runs showed it to be in excellent shape.

The last burner grid developed was of similar design but screwed onto the burner tube, so that the delicate studs could be eliminated. The mesh flame arrester was not welded to the burner tube but was seated on a shoulder cut into the wall of the burner tube at its top. Performance of this new burner has been excellent. It ignites easily, even at elevated pressures, the flame is stable over almost all operating conditions, and it should have a very long life expectancy.

COOLING COILS

The combustor contained three pair of serpentine wound cooling coils which extended from about 6 inches above the fluidizing grid upwards for about 6 feet. The coils were made from 1/4 inch diameter stainless steel tubing and had a total surface area of about 6.3 sq. feet. Each pair was centered at a flange so that one coil could be removed without disturbing the others.

Water flow into each pair of coils was independently controlled. House water was demineralized before its pressure was increased with a pump. The water flow then split into three branches which connected with the cooling coils. Each branch contained a rotameter followed by a metering valve. The branch connecting with the middle pair of coils also contained an automatic control valve which could be used instead of the manual valve.

During the first runs with the combustor, house water entered the cooling system at about 40 psig and no pump was used to increase pressure further. With this arrangement, control over the amount of water entering the coils was unsatisfactory. Because of expansion produced during the formation of steam, back pressures greater than the inlet pressure of the water developed in the coils.

This resulted in water entering the coils one slug at a time, a limit to the maximum amount of water that could be fed into the coils, and very little control over the flow rate of water.

It should be noted that it was not feasible to control heat removal from the combustor by using enough water to maintain single phase flow. This is because the rate of heat removal is proportional to the log mean ΔT, which would be nearly constant over the range of flowrates required to maintain single phase flow. Also, the use of air as a cooling medium had been investigated, but the flow of air required to keep the coil temperature at a safe level would be so high as to remove an excessive amount of heat from the bed.

Control over water flowrate was improved by increasing the inlet pressure of the water by means of a pump. This created a much larger pressure drop across the control valve than existed previously. With increased pressure drop, downstream pressure fluctuations affected flowrate less. Initially, inlet pressure was increased to 150 psig; but this pressure was not high enough and a Delavan Model 20001 piston pump was then installed. This pump can deliver two gallons/min. at pressures up to 500 psig; however, because of pressure limitations on the rotameters, operation was limited to about 300 psig. Fluctuations in water flow were greatly reduced and control over water flowrate was satisfactory with water inlet pressure at this value.

COMBUSTOR CYCLONES AND FILTER

Two cyclones normally removed flyash and entrained solids from the combustor. It was found; however, that during the first several minutes of some combustion runs, temperatures at the cyclones were not high enough to prevent condensation of steam from the off-gas. When this occurred, efficiencies of the cyclones were reduced sufficiently to allow flyash to reach the system filter. The filter then plugged rapidly, disturbing the pressure in the combustor, the pressure drop from the coal feeder to combustor, and the flow of coal.

The problem to be solved was to prevent the filter from plugging with flyash. The easiest solution was to add an electrical heater and a third cyclone downstream of the first two cyclones. The heater was used during the early stages of runs to keep the temperature of

the off-gas entering the third cyclone above its dew point, so that this cyclone could effectively remove flyash from the off-gas. This system worked well although it was needed on only several occasions when steam condensation was a problem.

REGENERATOR BED HEATERS

The lower section of the regenerator contained two 15 KW electrical heaters which were used during startup to bring the bed up to the desired temperature more rapidly than was possible with the propane burner alone. The heaters also smoothed the temperature distribution over the fluidized bed by increasing temperatures in the upper portion of the bed.

The heaters were constructed from resistance wire which was wrapped around the alumina reaction tube located in the center of the shell of the regenerator. Two layers of "Fiberfrax" insulation surrounded the windings to provide a cushion for thermal expansion. The annular space between the alumina tube and the inside of the steel shell was filled with castable refractory insulation.

A temperature runaway in the bed of the regenerator occurred during the first run and the heater windings were destroyed. New heaters were installed which lasted for eight runs. The heaters were examined and it was concluded that failure was caused by a combination of corrosion and overheating. Corrosive gases could have worked their way through cracks in the alumina reaction tube and contacted the heater windings. A new alumina tube plus a new set of heater windings were installed. The lower 10 inches of the tube was made removable so that it could be easily replaced if it cracked. It was decided to operate the new heaters at reduced power to minimize the possibility of overheating.

Unfortunately, the new heaters failed after only two runs. Failure was attributed to chemical attack by reducing gases and SO_2. It was decided not to re-install heaters as no simple way was known to prevent corrosive gases from reaching the heater windings.

OFF-GAS COOLERS

Heat exchangers were used to cool off-gases from the regenerator and combustor to temperatures just above their dew points. The original unit used with the regenerator was an American Standard shell-and-tube heat exchanger with ninety-1/4 inch stainless steel tubes through which gas flowed. The off-gas cooler had to be removed from the system when it was discovered that a number of tubes had cracked. Examination of the unit showed that some tubes had developed radial cracks and that many of the tubes were plugged with solids. The cause of the cracks was attributed to differences in thermal expansion between the tubes and a ceramic header, located near the gas inlet.

Heat transfer calculations, based on experimental data, indicated that the original exchanger had too much area. As a result, the exchanger was rebuilt using three 1/2 inch stainless steel tubes inside the original shell. No problems have since developed in over eight months of operation.

The heat exchanger used with the combustor contained nine 1/4 inch diameter (.049 inch wall) tubes of 304 stainless steel. Gas flowed through the tubes. No operating problems have developed in about five months of operation.

MATERIALS OF CONSTRUCTION

After the fluidized bed regenerator was started up, a number of materials problems developed caused by the combination of high temperatures and the chemical environment.

Fluidizing Bed Grids

The original fluidizing bed grid used in the regenerator was made of cast alumina. In the first few runs made in the regenerator, high temperatures occurred which resulted in melting of the bed charge, apparent reaction of the molten charge with the grid and cracking of the grid. The grid was destroyed in these runs. A photograph of the fused material and the grid is shown in Figure 19. Analysis of the molten material indicated the presence of $CaSO_4$, CaO and $Ca_3Al_2O_6$.

Examination of the phase diagram of the CaO-Al_2O_3 system indicated that a melt of calcium oxide and calcium aluminate could exist at temperatures as low as 2550°F. Apparently, CaO was reacting with the alumina grid to form the oxide-aluminate mixture which melted at the lower temperatures. An additional run was made with an alumina grid under lower and better controlled bed temperatures conditions. Although the damage to the grid was much less, it still showed some signs of reaction with the bed charge, was bowed upward and cracked. A cast zirconia grid was then fabricated and tested. Zirconia not only has a higher melting point than alumina but also forms no low melting point mixtures with CaO. The zirconia grid showed no signs of reaction with the bed material, but was still slightly bowed and cracked. In order to impart maximum strength to the zirconia it must be cured at 3000°F. Available curing ovens could only cure at 400°F and the grids were therefore, not cured to maximum strength. Also, no assurance could have been given that the fully cured zirconia could stand up to the repeated oxidizing-reducing cycles in the regenerator. Therefore, it was decided to abandon the concept of cast ceramic grids and fabricate the water cooled stainless steel grid described in Section IV.

The water cooled steel grid has worked very well after some early problems of water leakage at a welded joint were solved. The grid was examined after being in operation for a number of months. The only apparent sign of damage was a small raised section which may have been caused by a blocked cooling channel.

Figure 19. Fused regenerator bed material and fluidizing grid

Ceramic Reactor Liner

Melting and fusion of the bed charge in the regenerator which destroyed the alumina fluidizing grids also severly damaged the mullite ceramic bed liner. Mullite is an impure alumina, containing a significant amount of silica. It was believed that low melting silicate systems could have formed by reaction of the liner with the molten bed charge. Since the silicates have even lower melting points than aluminates, it was decided to replace the mullite liner with an alumina liner. The alumina reactor showed no signs of reaction with the bed material during succeeding runs. However, due to its poorer resistance to thermal shock, the alumina tube cracked and had to be periodically patched with ceramic cement.

Refractory Insulation

The Litecast 7528 refractory insulation used in the regenerator and combustor vessels has held up very well with use. The only damage sustained by the refractory occurred in the regenerator when the bed charge melted and attacked the ceramic liner and portions of the refractory also. Since the problem of bed charge melting was solved, no further damage to the refractory has occurred.

The Bubbalite high temperature refractory used in the burner zones of the combustor and regenerator has also held up very well. The only damage sustained so far occurred when a failure in the regenerator burner caused direct flame impingement on the refractory. This resulted in the melting of a small portion of the refractory but was easily repaired by patching.

SECTION VI

EXPERIMENTAL RESULTS

COLD MODEL TEST UNIT

Effect of Simulated Steam Coils on Fluidization Characteristics

Tests were conducted to determine the internal baffling effect of the simulated coil upon the fluidizing and slugging character of the bed, and the anticipated particle entrainment. The tests were conducted in the combustor section of the CMTU over the following range of parameters:

Superficial Bed Velocity (ft/sec)	4, 6, 8, 10, 12
Settled Bed Height (ft)	2, 2.5, 3, 3.5, 4
Vessel Pressure (psia)	20, 30, 40, 60

It was visually observed that the simulated coils inserted in the acrylic model produced a well fluidized bed, especially in the region where the expanded bed is below the upper coil level. It is therefore anticipated that this type of coil configuration will promote very satisfactory mixing and heat transfer in a high temperature combustor.

Test results indicated that expanded bed height increases with increasing settled bed depth, pressure and superficial bed velocity (Fig. 20 and 21). Thus the tendency toward slugging and high entrainment rates is increased by operating with deeper beds, higher velocities and higher pressures.

The insertion of the simulated coils, in addition to improving the bed fluidization behavior, also significantly reduced the slugging nature of the fluid bed (Fig. 22). For example, with a 3 feet settled bed at 40 psia and a superficial bed velocity of 6 feet/sec., the average expanded bed height was reduced from 132 inches to 78 inches when the simulated coil was inserted.

This implies that the coils provide a modulating or baffling effect and that combustor outage height can be reduced without an increase in particle entrainment.

Determination of the minimum fluidizing velocity was also obtained by increasing the fluidizing air velocity until the bed particles were just visually fluidized. The results indicated that the minimum fluidizing velocity is not affected by bed depth and decreases with increasing reactor pressure (see Fig. 20 and 21).

Figure 20

Effect of superficial bed velocity on expanded bed height

2 ft. settled bed, simulated heat transfer coil

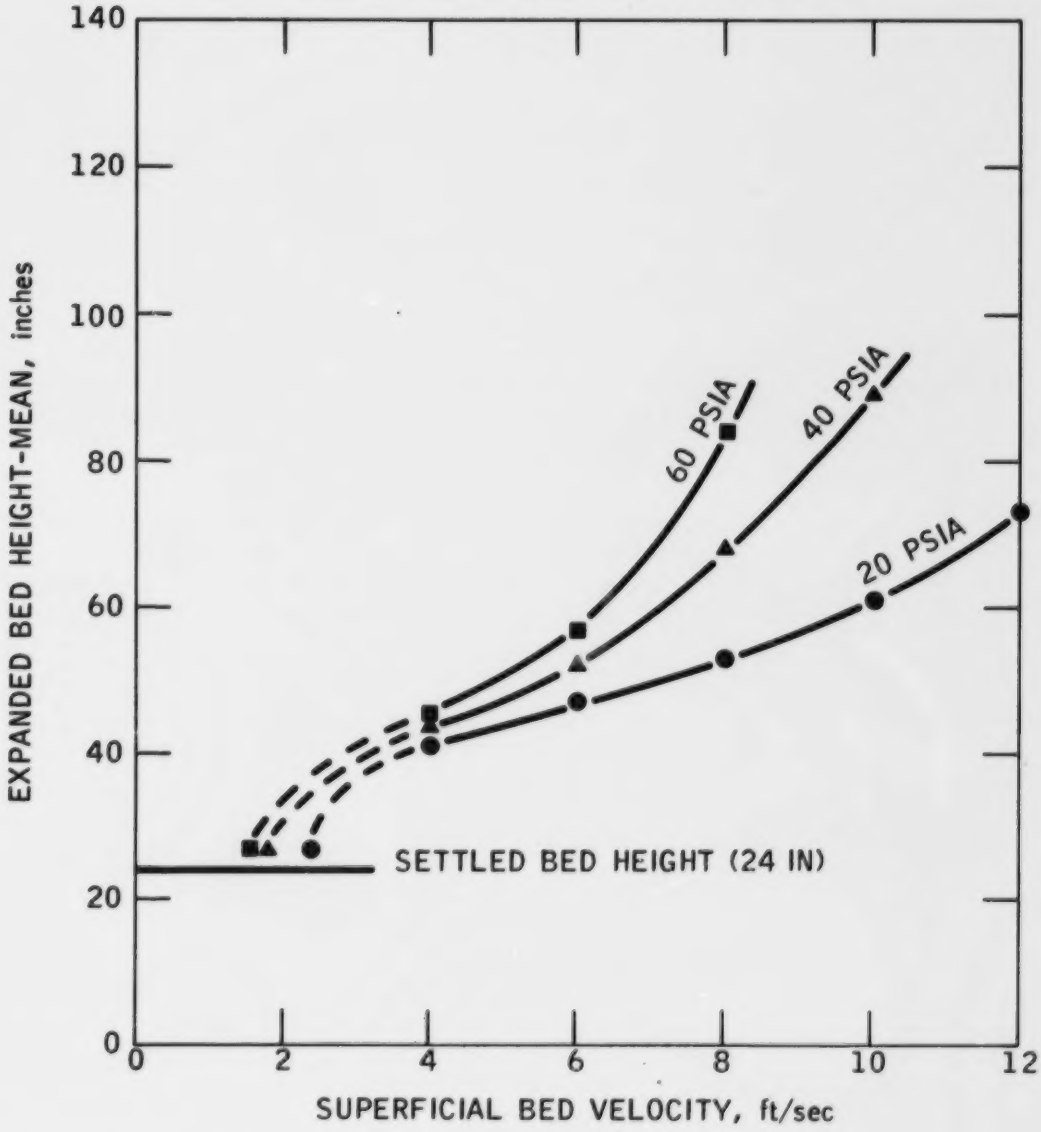


Figure 21

Effect of superficial bed velocity on expanded bed height

3 ft. settled bed, simulated heat transfer coil

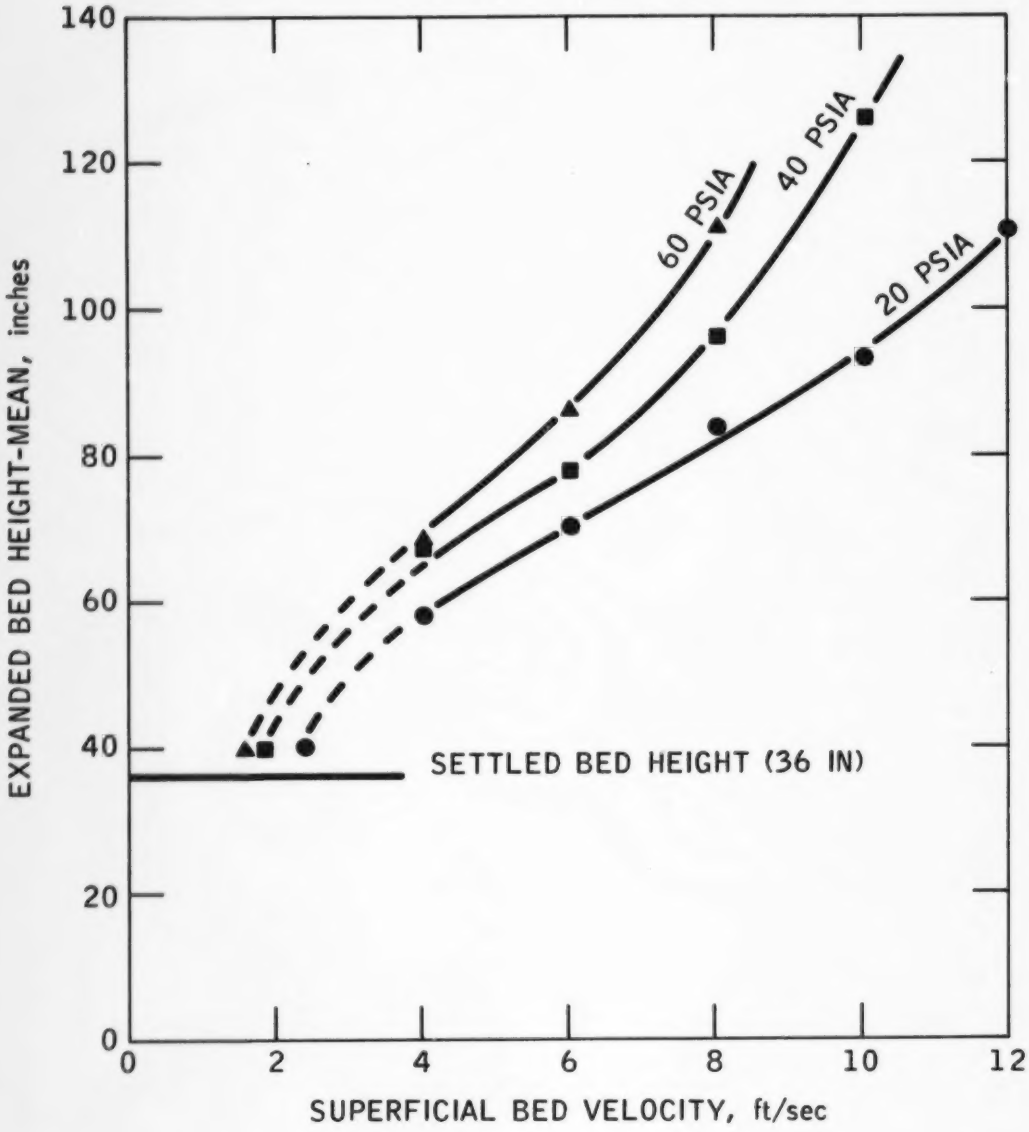
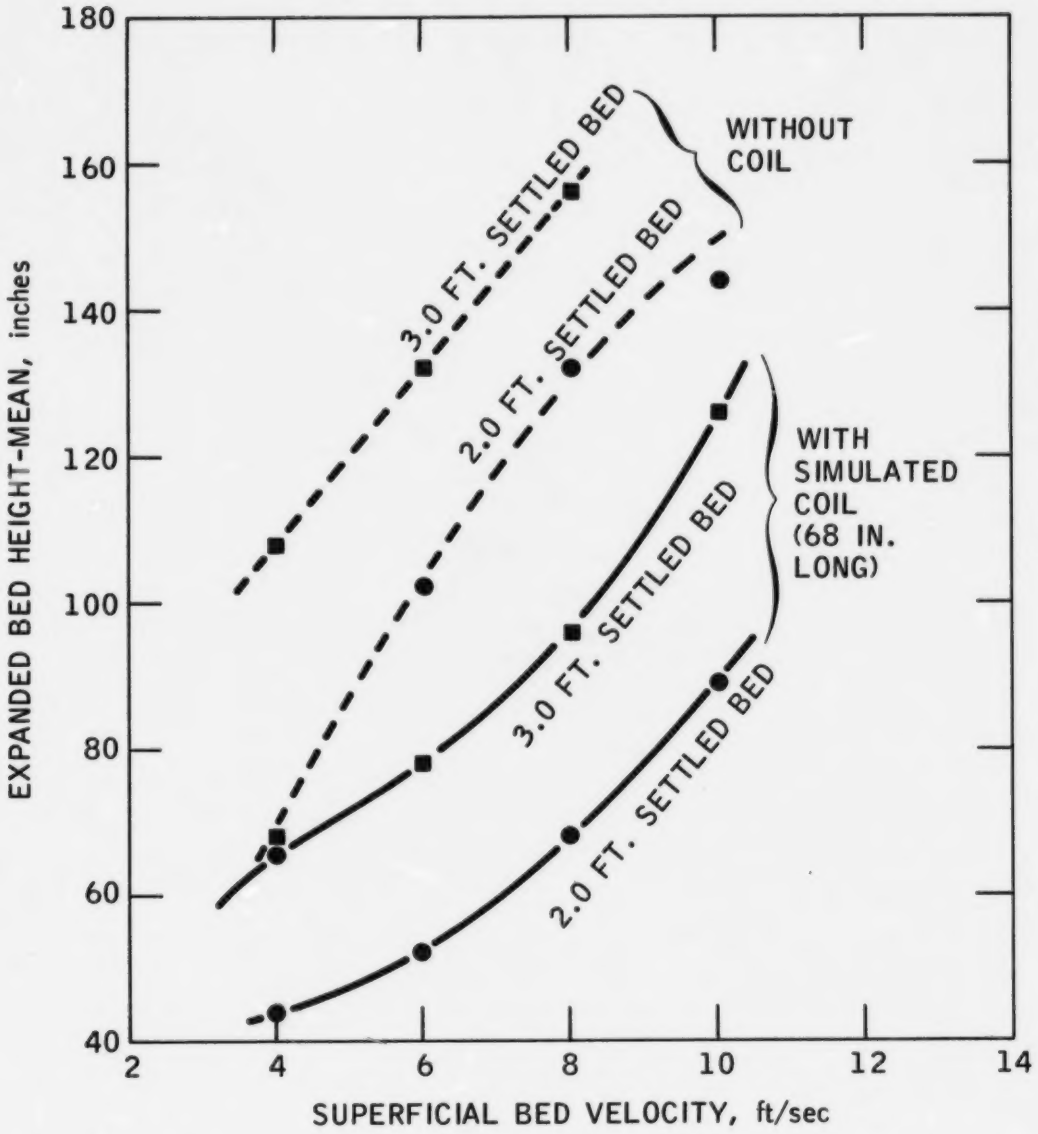


Figure 22

Effect of heat transfer coil on expanded bed height

40 psia Pressure



The minimum fluidizing velocity is considered to be most likely a function of fluidizing gas density rather than just pressure. Since the tests were run at the same temperature, the density varied directly with the pressure. At 20 psia, for the stone particle size distribution used, the minimum fluidizing velocity is 2.4 ft/sec; at 60 psia it is 1.6 ft/sec. It should be noted that the same density effect is also most likely true for the cases involving the expanded bed height. That is, it is probably the density of the fluidizing air, rather than just the reactor pressure, that influences the expanded bed height of the fluidized system.

Continuous Transfer of Solids

Studies were conducted in the Cold Model Test Unit to determine the effect of various parameters upon the solids transfer rate between prototype reactors and to measure this transfer rate.

Tests were conducted at reactor vessel pressures to 40 psia, with settled bed heights of 3.0 feet. Since the solids were transferred using the pulse air technique, the main parameters varied were pulse air flow rate and pulse frequency, i.e., pulse on/off cycle. The results of the two-way transfer runs at 40 psia are presented in Figure 23.

The tests verified the ability of the continuous system to transfer solids in both directions while operating under pressure and maintaining good bed level control in both vessels. Transfer rates of 6.1 lb/min were attained while transferring solids continuously in both directions at 40 psia vessel pressure. The rate of solid transfer between vessels was controlled by varying the pulse cycle and also the pulse air flow rate.

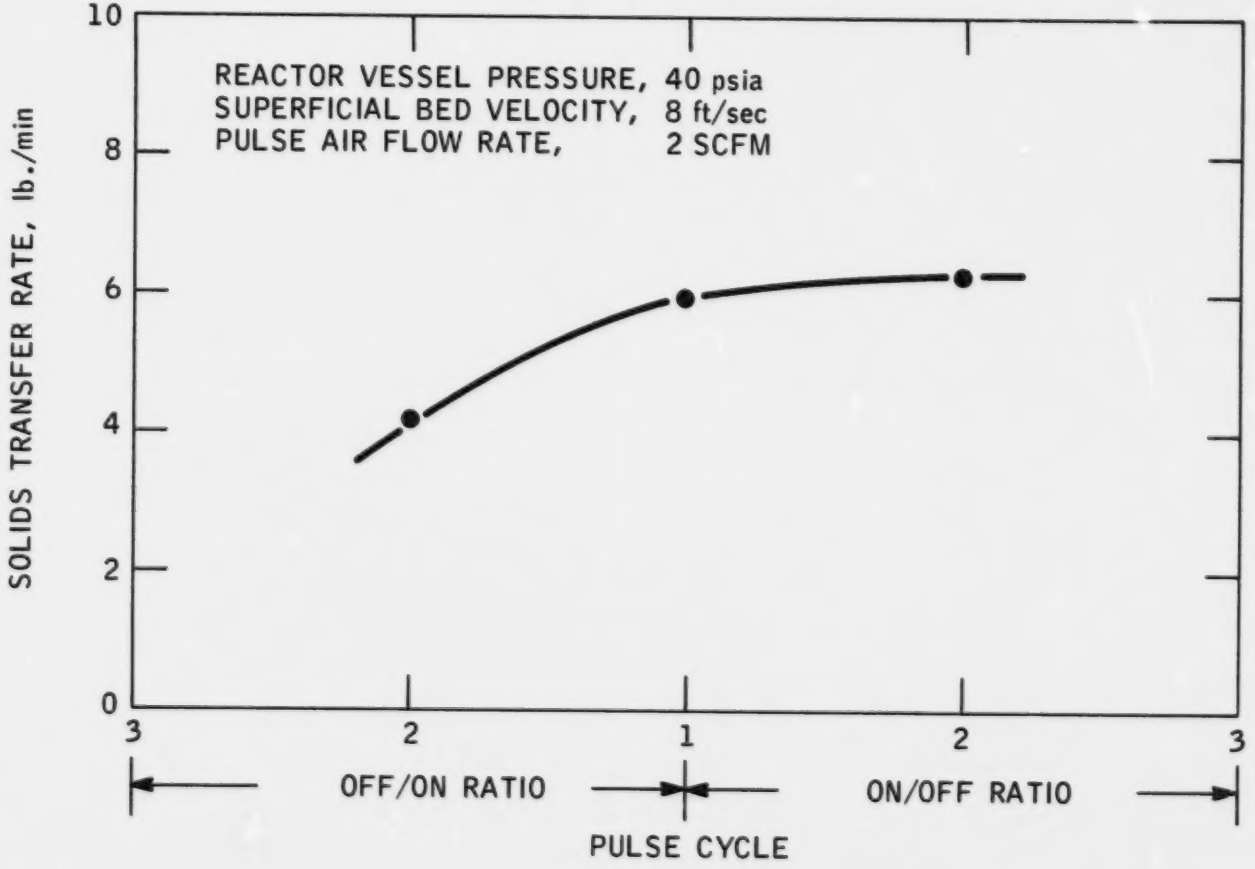
Observations of the continuous transfer operations in the CMTU indicated that the 1-inch I.D. catch tube inserted in the prototype combustor was a limiting or choking restriction on the maximum transfer rate attainable. However, the solids reservoir installed in the prototype regenerator (Figure 2) functioned satisfactorily in that it permitted freer solids flow and a superior transfer line seal than the catch tube. When transferring solids in one direction, from regenerator to combustor, solids transfer rates as high as 9.9 lb/min were attained. This is attributed to the ample sizing and configuration of the regenerator transfer reservoir.

Transfer line fittings and restrictions not only limit the solids flow rate, but induce hold-ups and plugs in the transfer line. As these line restrictions in the CMTU were systematically eliminated, improved solids transfer rates were achieved.

It is anticipated that with adequate pipe line sizes and a minimum of restrictions, the Miniplant will be able to achieve satisfactory solids transfer with this pulse technique. The Miniplant transfer rate design is 680 lb/hr (11.3 lb/min) under maximum conditions.

Figure 23

Solids transfer rate



COMBUSTION STUDIES

Fluidized Bed Combustion Unit

Because of operating problems coal has not been fed continuously into the batch combustor for more than about twenty minutes at a time. These problems involved poor control over the flow of water entering the cooling coils, heavy accumulation of flyash in the off-gas filter, and unsatisfactory operation of the coal feeding system. The first two difficulties have essentially been resolved and progress has been made toward improving the operation of the coal feeding system. The last major obstacle appears to be preventing plugging in the coal probe and orienting the probe so that coal burns uniformly throughout the fluidized bed.

Table 6 presents operating parameters for coal combustion runs. The compositions of effluent streams are given in Table 7. When evaluating this data, it is important to recognize that, because coal was fed only for brief periods, conditions in the combustor (e.g. coal feed rate, temperature, off-gas composition) were unsteady. Because there were problems with control of temperature, and also with the feeder, coal rates had to be kept low. As a result, excess air levels were far higher than they would normally be.

Calcination of Limestone and Dolomite

A 23 lb. charge of Grove #1359 limestone was calcined in the combustor in about one hour at an average temperature of 1560°F. It was desirable to calcine in the combustor because this eliminated the need to transfer stone to the combustor from the vessel in which it was calcined.

A nearly stoichiometric air-propane mixture was used and the superficial velocity was 8-10 ft./sec. The total pressure was about 2.6 atm; the CO_2 concentration in the off-gas was approximately 21%. At the conclusion of calcination the bed temperature rose to 1700°F and the level of CO_2 in the off-gas fell to 15%, about the same level of CO_2 as observed before calcination. The combination of temperature rise (due to the end of endothermic calcination) and drop in CO_2 concentration gave a definite indication of the completion of calcination. Subsequent chemical analyses showed that more than 99.9% of the carbonate had been converted to oxide.

Subsequently, a 16.6 lb. batch of -8 + 25 mesh Tymochtee dolomite was half-calcined by heating in the combustor for about six hours at 1200-1400°F. Proper half-calcination should have produced a material containing only $CaCO_3$ and MgO. Subsequent analysis of solids showed that some decomposition of the calcium portion of the stone had also occurred:

83 wt. % ($CaCO_3$ + MgO)
17 wt. % (CaO + MgO)

Table 6. OPERATING PARAMETERS - COAL COMBUSTION RUNS

Run No.	Charge, material, lbs.	Settled bed height, ft.	Press., psig	Superficial velocity, ft./sec.	Input Coal, lb/hr	Input Air, SCFM	Average bed temperature, °F	% Excess air[c]
66-2690-112a	limestone, 23	2.0	103	3.9	13.3[a]	43.5	1480 ± 100	43
66-2690-112b	limestone, 23	2.0	103	4.3	15.5[b]	43.5	1660 ± 100	23
66-2690-127	dolomite, 16.6	2.0	63	5.4	8.6	40.0	1480 ± 100	104
66-2690-128a	dolomite, 16.6	2.0	63	5.8	7.2	41.5	1560 ± 100	153
66-2690-128b	dolomite, 16.6	2.0	104	5.6	8.8	62.0	1510 ± 100	209
66-2690-128c	dolomite, 16.6	2.0	104	6.1	9.2	63.5	1640 ± 100	203

Coal: Arkwright Mine, -30 mesh
Limestone: Grove #1359, -7 mesh, calcined.
Dolomite: Tymochtee, -8+25 mesh, half-calcined.

[a] Average coal rate varied over range of 10.0-18.0 lb./hr.
[b] Average coal rate varied over range of 15.0-17.1 lb./hr.
[c] $\%\ \text{Excess air} = \frac{\text{Actual air - stoichiometric air}}{\text{Stoichiometric air}} \times 100$

Table 7. COMPOSITION OF EFFLUENT STREAMS - COAL COMBUSTION RUNS

Run No.		66-2690-112a			66-2690-112b	
		Measured[c]			Measured	
	Calc.	Avg.	Range	Calc.	Avg.	Range
SO_2, ppm	1540[a]	240	steady	1780	250	steady
NO, ppm	--	310	230-370	--	290	150-380
CO_2, %	12.0	10.6	6.5-19.0	13.9	13.5	5.2-23.6
CO, %	--	0.9	0.1-2.0	--	0.7	0.1-2.7
H_2O, %	5.0	not collected		5.8	not collected	
O_2, %	6.0[b]	9.6	3.3-15.5	3.7	7.6	1.9-15.4
N_2, %	76.8	--	--	76.5	--	--
SO_2 Removal[d] (%)		84.4			86.0	

Run No.		66-2690-127			66-2690-128a	
		Measured			Measured	
	Calc.	Avg.	Range	Calc.	Avg.	Range
SO_2, ppm	1100	145	100-140	900	250	125-550
NO, ppm	--	340	160-550	--	450	250-550
CO_2, %	8.5	7	3-11	6.9	7.0	4.5-9.5
CO, %	--	.03	.02-3.0	--	.03	0.01-1.0
H_2O, %	3.5	not collected		2.9	not collected	
O_2, %	10.4	12	2-17	12.4	10	3-15
N_2, %	77.5	--	--	77.7	--	--
SO_2 Removal (%)		86.8			72.2	

Table 7 (continued). COMPOSITION OF EFFLUENT STREAMS - COAL COMBUSTION RUNS

Run No.	66-2690-128b			66-2690-128c		
		Measured			Measured	
	Calc.	Avg.	Range	Calc.	Avg.	Range
SO_2, ppm	700	320	225-550	700	320	100-600
NO, ppm	--	380	350-430	--	340	170-490
CO_2, ppm	5.7	8.0	7.5-9.5	5.7	8.0	5.0-11.5
CO, %	--	.03	.01-0.4	--	.02	.01-.4
H_2O, %	2.4	not collected		2.4	not collected	
O_2, %	13.9	9	5-14	13.9	11	5-17
N_2, %	78.0	--	--	78.0	--	--
SO_2 Removal (%)			54.3			54.3

[a] Assumes no SO_2 removed in bed.
[b] Assumes all $C \longrightarrow CO_2$ and $H \longrightarrow H_2O$.
[c] Corrected for water condensed prior to analysis.
[d] SO_2 removal = $\frac{\text{Calculated } SO_2 - \text{observed } SO_2}{\text{Calculated } SO_2} \times 100$.

SO_2 Removal

In two runs (112a, 112b) made with calcined Grove limestone, SO_2 removal was 84.4 and 86.0%. It was estimated that conversion of CaO to $CaSO_4$ in the bed was 2.0% prior to run No. 112a and 5.4% after run No. 112b. The combined coal feeding time for these runs was 47 minutes; 11.5 lbs. of coal were burned.

Several brief runs were made with half-calcined Tymochtee dolomite; a total of about 15 lbs. of coal were burned, which corresponds to a conversion to sulfate of about 10%. It can be noted in Table 7 that the percentage of sulfur removal decreased with each subsequent run. This is probably due to loss of dolomite through attrition, which appeared to be very high, rather than to deactivation caused by sulfate loading.

Even during the first combustion run with dolomite (127) sulfur removal was only 87%. This is not surprising in light of poor temperature control. Table 6 shows that the bed temperature for this run was 1480 $\pm$ 100°F. It was not possible to determine an average bed temperature more precisely because of large temperature changes during the run and steep temperature gradients in the bed. Poor temperature control was due to inadequate flow of water through the cooling coils, unsteady coal flow, and combustion of most of the coal in the immediate vicinity of the coal inlet point. Progress has been made to correct these problems.

NO_x Levels

Average concentrations of NO_x were typically 300-400 ppm although the instantaneous concentration fluctuated widely because the coal feed rate was unsteady. NO_x concentrations would undoubtedly have been considerably lower had it not been for the high levels of excess air, which averaged between 23 and 209 percent.

Attrition

Attrition during runs with calcined Grove limestone appeared to be fairly low; however, attrition was very high during runs made with half-calcined Tymochtee dolomite. With the latter material, about one-half of the bed wound up as fines in the cyclone diplegs. Reasons for the high attrition rate are being examined to determine if the stone, as it appears to be, or equipment (or both) was responsible.

Fixed Bed Units

Reaction of CO and NO under Simulated Combustion Conditions -

The reaction of CO and NO under simulated combustion conditions was studied in the stainless steel fixed bed reactor. This study was carried out to extend earlier work which had identified this reaction as one which could be responsible for reduced NO_x emissions observed in the fluidized bed combustion of coal. Calcined limestone (No. 1359) or dolomite (No. 1337) was used as bed material. In the study, pressures were held at 1 or 10 atm, temperature was 1600°F. Premixed gases were blended to maintain the CO and NO levels at either approximately 1000 or 2000 ppm each. The CO_2 level was held at 0 or about 15%, the O_2 level was held at 0 or about 2.5%. Residence time at 1 atm pressure was held constant at 0.3 sec. At 10 atm pressure, residence time was varied from 0.4 to 3 sec by varying the feed gas flow rate. However, at residence times below about 0.5 sec, the flow rate was too high to maintain the temperature at 1600°F and the temperature fell to 1400°F at the highest flow rate studied. A summary of the runs is given in Appendix Table A-1.

In the absence of CO_2, the reaction between CO and NO proceeds to 95-99% of the limiting reactant over calcined limestone or dolomite. This is shown in Table 8. The reaction proceeds in a 1/1 molar ratio of CO and NO, suggesting the reaction

$$2CO + 2NO \longrightarrow 2CO_2 + N_2 \qquad (3)$$

As seen in Table 8, when CO_2 was added, conversion of the limiting reactant decreased to 19-26%. The effect of CO_2 was almost instantaneous. In one case, the CO_2 blend was cut out of the feed and the flow of the CO/NO blend was increased to maintain a constant feed rate. The NO concentration fell from 625 ppm to 63 ppm in about 1 minute and then decreased more slowly to 22 ppm over the next 10 minutes. The lag time for the sampling and analytical system was measured at 50 sec, so the response of the system to the removal of CO_2 was virtually instantaneous.

TABLE 8. NO-CO REACTIONS

Bed Source	CALCINED LIMESTONE #1359			CALCINED DOLOMITE #1337		
Inlet Gas Comp.						
NO, ppm	1400	1800	860	1400	1990	840
CO, ppm	940	1870	990	900	2080	980
CO_2, %	0	0	17	0	0	16
Outlet Gas Comp.						
NO, ppm	400	20	640	350	240	680
CO, ppm	10	160	770	20	100	830
CO_2, %	0	0	17	0	0	17
Conv., %	99	99	26	98	95	19

Temperature: 1600°F

Res. Time: 0.3 Sec.

The effect of pressure was studied and, although increasing the pressure to 10 atm in the presence of CO_2 apparently increased the conversion, the increase was probably due to increased residence time. At equivalent residence times, increasing pressure appeared to decrease the conversion slightly. This is shown in Table 9.

TABLE 9. NO-CO REACTIONS
EFFECT OF PRESSURE AND RESIDENCE TIME

Bed Source	CALCINED LIMESTONE #1359			CALCINED DOLOMITE #1337	
Press. (Atm.)	1	10	10	1	10
Res. Time (Sec.)	0.3	3	0.3	0.3	3
Inlet Gas Comp.					
NO, ppm	860	890	1150	840	840
CO, ppm	990	980	1240	980	980
CO_2, %	17	18	13	16	16
Conv., %	26	82	16	19	88

Temperature: 1600°F

Changing the background gas from N_2 to argon appeared to increase the conversion very slightly, but the effect may not be significant. O_2 was added to the feed and appeared to increase conversion slightly. This is shown in Table 10.

TABLE 10. NO-CO REACTIONS
EFFECT OF O_2

Bed Source	CALCINED LIMESTONE #1359		CALCINED DOLOMITE #1337	
Inlet Gas Comp.				
NO, ppm	1150	970	840	980
CO, ppm	1240	1060	980	1080
CO_2, %	13	16	16	15
O_2, %	0	2.4	0	2.3
Conv., %	84	95	88	91

Temperature: 1600°F

Pressure: 10 Atm.

Increasing the temperature from 1600 to 1700°F in the presence of CO_2 at 1 atm pressure had essentially no effect on conversion.

The reason for the large CO_2 inhibiting effect is not understood. Carbonation of lime was considered but does not explain the effect since CaO does not carbonate at the conditions used in the 1 atm runs. At these conditions the inhibiting effect was pronounced. Carbonate is the stable form at 10 atm pressure and 1600°F but the oxide is the stable form at 1700°F. However, changing reaction temperature from 1600 to 1700°F at 10 atm had no effect on conversion. Inhibition by chemical reversibility was also considered, but does not explain the results. The most likely explanation for this effect is a kinetic limitation caused by the presence of the CO_2.

REGENERATION STUDIES

Introduction

A gas containing CO and H_2 can reduce calcium sulfate to the oxide at high temperatures. The reactions are

$$CaSO_4 + CO \longrightarrow CaO + SO_2 + CO_2 \quad (4)$$
$$CaSO_4 + H_2 \longrightarrow CaO + SO_2 + H_2O \quad (5)$$

Formation of CaS, via side reactions, is undesirable because large amounts of reductant are used and no SO2 is produced:

$$CaSO_4 + 4CO \longrightarrow CaS + 4CO_2 \quad (6)$$

$$CaSO_4 + 4H_2 \longrightarrow CaS + 4H_2O \quad (7)$$

$CaSO_4$ can react with CaS to produce CaO but this reaction does not occur to a great extent:

$$3CaSO_4 + CaS \longrightarrow 4CaO + 4SO_2 \quad (8)$$

Reactions (4), (5), and (8) are favored by high temperatures whereas (6) and (7) are favored at lower temperatures. Gas composition has an effect through CO/CO_2 and H_2/H_2O ratios. High ratios promote reactions (4) and (5) but promote reactions (6) and (7) to an even greater extent.

There are at least nine process variables which can affect the performance of the regenerator. These are:

1) pressure
2) temperature
3) air/fuel ratio (concentration of CO + H_2 in reducing gas)
4) space velocity (superficial velocity/bed depth)
5) manner of fuel introduction and use of auxiliary fuel
6) use of auxiliary air
7) particle size of bed material
8) nature of bed material (pure $CaSO_4$, sulfated limestone or dolomite)
9) quality of fluidization

To evaluate the overall performance of the regenerator several factors must be examined. The most important is concentration of SO_2 in the off-gas, which, of course, is to be maximized. Concentration can be considered both as an absolute molar percentage or as a percentage of the maximum concentration which is possible at equilibrium. Another index of performance is the conversion of $CaSO_4$. Even a high concentration of SO_2 is not alone sufficient to make performance of the regenerator acceptable if only a small fraction of the $CaSO_4$ charged has been regenerated. Moreover, $CaSO_4$ can be reduced to CaS and CaO. It is desired to minimize the ratio of CaS/CaO in the regenerated product. Other indices of performance include the degree of attrition of the bed and the uniformity of temperatures in the bed (an indication of the quality of fluidization and gas-solids contacting).

Fixed Bed Regeneration Studies

Prior to the construction of the high pressure batch regeneration unit, a few regeneration runs were made in the ceramic tube fixed bed regeneration unit at pressures between 1 and 9.5 atm. This work was done primarily to measure SO_2 product concentrations at the higher pressures. Temperatures were held at 1900 or 2000°F. Anhydrous $CaSO_4$ (Drierite) and

sulfated limestone were used as bed materials. The reducing gas feed was blended from CO/N_2 and CO_2/N_2 mixtures to permit variation of the CO from 10 to 30% and the CO_2 from 10 to 20% in the feed. Gas linear velocities ranged from 0.16 to 1.45 ft/sec. corresponding to 20 to 150% of the calculated minimum velocity required to fluidize the beds. The results are given in Table 11. At lower pressures, 1 and 3 atm, SO_2 concentrations in the product peaked at about 7% using $CaSO_4$ beds. These concentrations correspond to 35 and 50% respectively of the SO_2 concentration calculated at equilibrium. However, when the pressure was increased to 9.5 atm, the SO_2 concentration dropped to 1.6% or 34% of the equilibrium level.

Two runs were then made with sulfated limestone obtained from earlier work at Esso and from the U.S. Bureau of Mines fluidized bed combustor. In these runs, the measured SO_2 concentrations were only about 0.5%, corresponding to about 10% of the equilibrium level. Moreover, the solids discharged from the reactor in the runs using sulfated limestone were partially agglomerated. This could have been due to softening of fly ash present in the sulfated limestone at regeneration temperatures. This could have then caused the bed to agglomerate in the absence of vigorous fluidization. The agglomeration may also have caused poor gas-solids contacting and low SO_2 product concentrations. Fixed bed studies were terminated at this point to permit operation of the batch, fluidized regenerator unit.

Fluidized Bed Regeneration Studies

Table 12 is a summary of runs made with the batch fluidized bed regenerator. A more complete listing of the operating parameters and results for each run is given in Appendix Table A-2.

Agglomeration of Bed

The first runs made with the batch-fluidized regenerator resulted in fusion of the bed. Heat transfer calculations showed that temperatures on the top surface of the ceramic fluidizing grid could exceed the melting point of $CaSO_4$ (about 2650°F). Additional calculations showed that radiation errors could result in thermocouples indicating temperatures several hundred degrees below the true temperature of the reducing gases. As a result, gas temperatures could have been high enough to melt $CaSO_4$.

It was decided to replace the ceramic fluidizing grid with a water-cooled stainless steel grid. This would preclude the possibility of localized melting of $CaSO_4$ occurring when it contacted the hot surface of the grid. To reduce the temperature of the reducing gas, diluent nitrogen was added to the burner along with air and fuel.

Table 11. RUN SUMMARY-FIXED BED REGENERATION STUDIES

Bed mat'l.	Temp., °F	Press., atm	Feed % CO	Comp. % CO_2	Flow, SCFM	Vel. ft./sec	$\frac{V}{V_{mf}}$ (c)	Peak SO_2%	% of equil.
$CaSO_4$	1900	1	21	15	0.1	1.45	1.4	7.1	0.33
$CaSO_4$	2000	3	31	10	0.1	0.51	0.5	7.2	0.48
$CaSO_4$	2000	9.5	10	20	0.1	0.16	0.2	1.6	0.34
Sulf. Lime (a)	2000	9.5	10	20	0.1	0.16	0.2	0.6	0.13
Sulf. Lime (b)	2000	9.5	10	20	0.19	0.31	0.3	0.4	0.08

(a) Bureau of Mines source
(b) Esso source
(c) Velocity/minimum velocity to fluidize
Charge wt. = 40 gm except 60 gm in run 36
Particle size = -18+20 mesh

Table 12. SUMMARY OF RUNS WITH BATCH FLUIDIZED BED REGENERATOR
(-10+20 mesh $CaSO_4$ (Drierite) bed)

Run No.	Avg. temp., °F	Pressure, atm	Feed %(CO+H_2)	Product CO/CO_2	Settled bed height, ft.	Superficial velocity, ft/sec	Observed SO_2, %	Equil. SO_2, %	% of equil.
66-2690- 71	2040	3.1	2	0.013	2.8	2.7	3.4	12.9	26
72	1990	3.2	15	0.013	5.6	2.9	5.2	9.8	53
75	2100	6.2	9	0.016	5.4	5.4	7.5	11.3	66
78	1950	6.0	11	0.021	4.0	2.4	2.0	5.0	40
86	1870	6.0	15	0.026	4.0	2.4	1.8	3.8	47
89	1970	6.1	15	0.023	4.0	2.5	1.7	5.1	33
98	2030	9.0	15	0.021	2.0	4.0	3.1	6.7	46
100	2080	10	15	0.023	2.0	4.3	1.6	9.0	18
101	1920	10	14	0.017	2.0	2.0	1.1	2.7	41
105[b]	1800	10	14	0.013	2.0	1.8	0.7	1.9	37
109[b]	2030 ± 40	10	7	--	2.0	3.5	3.0	6.0	50
115	2050 ± 20	10	11	0.048	2.0	3.6	1.9	6.7	28
116	1840 ± 20	4.9	13	0.040	2.0	4.1	1.1	4.2	25
119[c]	2000 ± 20	10	10	0.064	2.0	3.5 - 2.9	1.5	4.6	33
120[d]	2020 ± 30	10	10	0.059	2.0	3.8	1.6[a]	5.4	29
121[e]	1900 ± 30	5.0	17	--	2.0	3.2	1.3[a]	5.1	25
122A[f]	1840 ± 20	5.0	13.5	--	2.0	2.6	0.54[a]	4.4	12
122B[f]	2000 ± 20	10	14	--	2.0	2.8	2.0[a]	4.6	44
123[f]	1970 ± 20	5.0	13.5	--	2.0	4.0	2.3[a]	7.0	33
124[g]	1940 ± 40	10	23	0.061	4.0	2.6	2.0[a]	2.8	72
125[fh]	1950 ± 30	10		0.16	2.0	3.0	0.62[a]	3.0	21
126[gj]	1880 ± 80	10		0.062	4.0	3.0	1.2[a]	2.4	50

[a] Corrected for N_2 added in aux. air.
[b] Run terminated after 5 min.
[c] Aux. air injected 12 inches above grid.
[d] Fuel injected 6 inches above grid.
[e] Aux. fuel 6 inches above grid, aux. air 34 inches above grid overall ϕ = 10.8.
[f] Aux. fuel 6 inches above grid, aux. air 42 inches above grid overall ϕ = 1.02 for 122A, .99 for 122B, 1.06 for 123.
[g] Aux. fuel 6 inches above grid, aux. air 54 inches above grid.
[h] Sulfated limestone (Bureau of Mines)
[j] -20+40 mesh $CaSO_4$ (Drierite)

Computer calculations (3) were made to determine the flow rates of air, fuel, and nitrogen required to achieve the desired reducing gas composition and temperature. Equilibrium gas composition and adiabatic flame temperature were found as a function of equivalence ratio, pressure, and per cent dilution of air with nitrogen. Calculations were made over the range of 0.8-2.0 equivalence ratio, 1-10 atm, and 0-75% nitrogen dilution (a 75% dilution means that 75% of the air is replaced by N_2). An equivalence ratio of 0.8 is typical of that used during pre-heating of the regenerator (oxidizing conditions). Under reducing conditions, the equivalence ratio is greater than one.

Figure 24 presents the major results of the computer study. Adiabatic flame temperatures are plotted as a function of the percentage of $CO + H_2$ in the reducing gas mixture for nitrogen dilutions of 0, 10, 15, 20, 25 and 50%. Lines of constant equivalence ratio ϕ are also shown. Curves indicating constant dilution are drawn as dashed lines between $\phi = 0.9$ and $\phi = 1.2$ because there is insufficient data in this region to draw the curves accurately. The actual maxima in temperature should occur at an equivalence ratio of slightly greater than 1. All the results of Figure 24 are for a total pressure of 8 atm. but no significant error would result if the data were used over the pressure range of 1 to 10 atm.

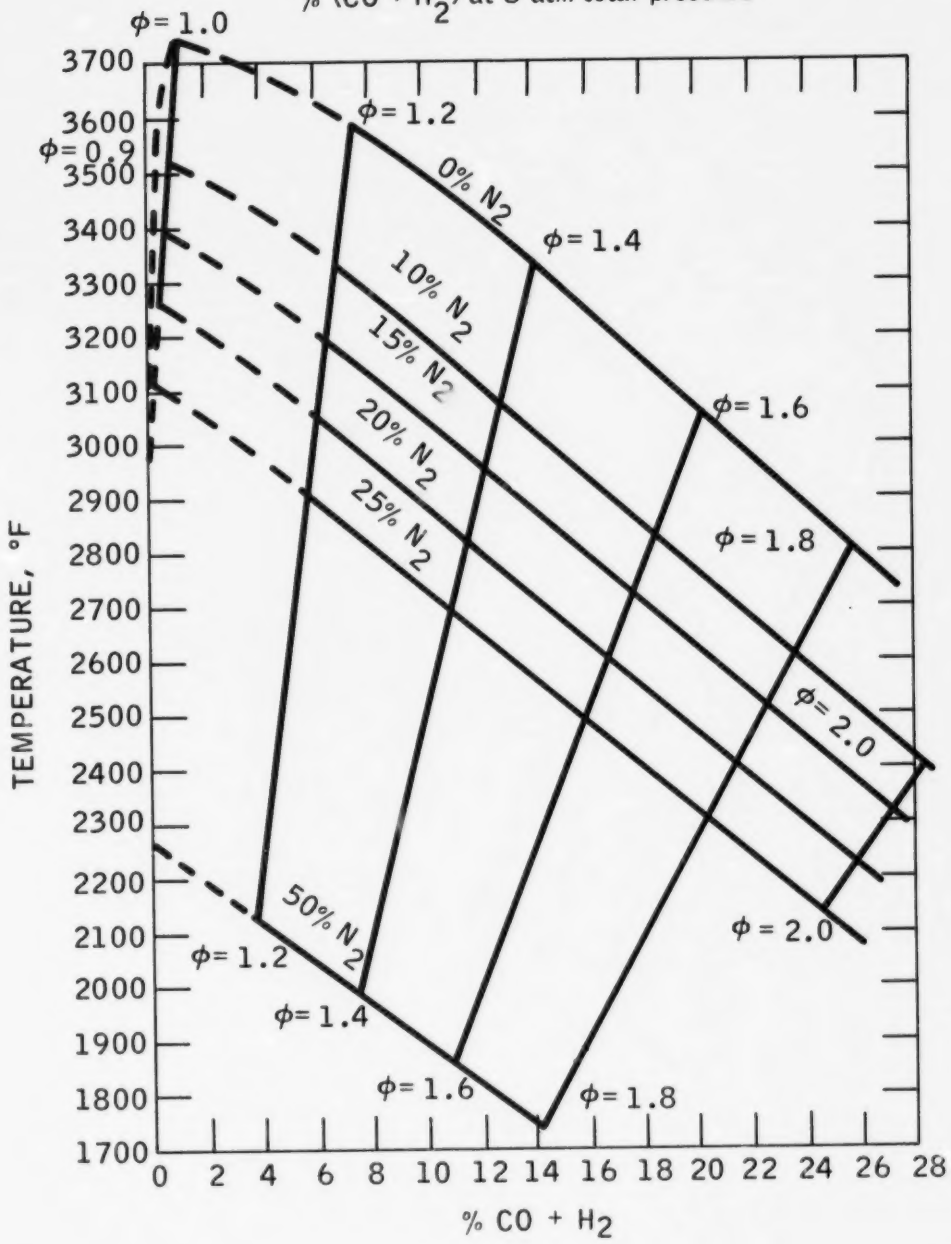
From experience with the regenerator, it was found that the adiabatic flame temperature had to be below about 2900°F to be certain that no melting of $CaSO_4$ would occur. Hence, Figure 22 was used to determine the percentage of nitrogen dilution and the air/fuel ratio required to prevent melting at whatever concentration of $CO + H_2$ was desired. The technique of diluting incoming air with nitrogen was found to be highly successful in preventing melting and agglomeration of the $CaSO_4$ bed.

Pressure

Runs were made over the pressure range of 3-10 atm. As pressure decreases, with superficial velocity constant, the amount of fuel added to the regenerator decreases. Hence, a minimum operating pressure exists which corresponds to a flow of fuel which is just sufficient to maintain the desired bed temperature. This pressure was about five atmospheres. The first runs were made at pressures of 3.1 and 3.2 atmospheres, respectively; however they were characterized by agglomeration and melting of solids and, as a result, there were very non-uniform temperature distributions in the bed. Thus, the average temperatures for these runs are not directly comparable to those reported for later runs, in which no agglomeration of solids occurred and in which temperatures were much more uniform. Also, somewhat higher air pre-heat temperatures were used in earlier runs (about 1000°F vs. 600-800°F for runs made later).

Figure 24

Adiabatic flame temperature versus
% ($CO + H_2$) at 8 atm total pressure



Use of pre-heated air produces higher bed temperatures but increases the likelihood of melting solids in the regenerator or causing a flashback into the tubular section of the burner if the self-ignition temperature of the fuel-air mixture is exceeded.

As the mole fraction of SO_2 in the regenerator off-gas increases, fuel costs for regeneration decrease. This provides an incentive to operate at low pressures because the mole fraction of SO_2 at equilibrium rises as the total pressure of the system is reduced. Hence, runs were made over a range of operating pressures. However, the percent approach to equilibrium was less at low pressures and, consequently, the mole fraction of SO_2 was not higher for runs made at low pressures than for runs made at higher pressures.

Figure 25 is a plot of concentration of SO_2, expressed as a percent of calculated equilibrium concentration, vs. pressure. If several runs are eliminated, for the reasons indicated in the figure, a trend can be observed toward increased approach to equilibrium at higher pressures.

Figure 26 is a plot of concentration of SO_2, expressed as a molar percentage, vs. pressure. The three runs with the highest SO_2 concentration were made early in the program and agglomeration of the bed occurred. Hence, temperatures in the bed were probably higher than indicated, which could account for high concentrations of SO_2. The remaining data do not show any significant effect of pressure on concentration. Presumably, at higher pressures, the closer approach to equilibrium compensated for the lower equilibrium concentration.

Temperature

Runs were made over the temperature range of 1800-2100°F. Figure 27 shows that the equilibrium partial pressure of SO_2 increases sharply with temperature in this range. Unfortunately, the risk of deactivating the solids by sintering, or deadburning, increases at higher temperatures, especially when the solids must undergo repeated cycles of sulfur absorption and regeneration. Hence, the optimum temperature for regeneration is the one which produces the maximum concentration of SO_2 over a number of cycles.

Temperatures in the fluidized bed were judged by thermocouples spaced six to twelve inches apart. The height of bed must be known to determine which thermocouples are located in the bed. Since this height could only be approximated, the temperature of the bed had to be estimated. Another reason why temperature could not be determined precisely was that it often changed during a run. When this occurred, an average with respect to time was taken to calculate an average temperature.

Figure 25

Regeneration studies - effect of pressure on approach to equilibrium SO_2 concentration

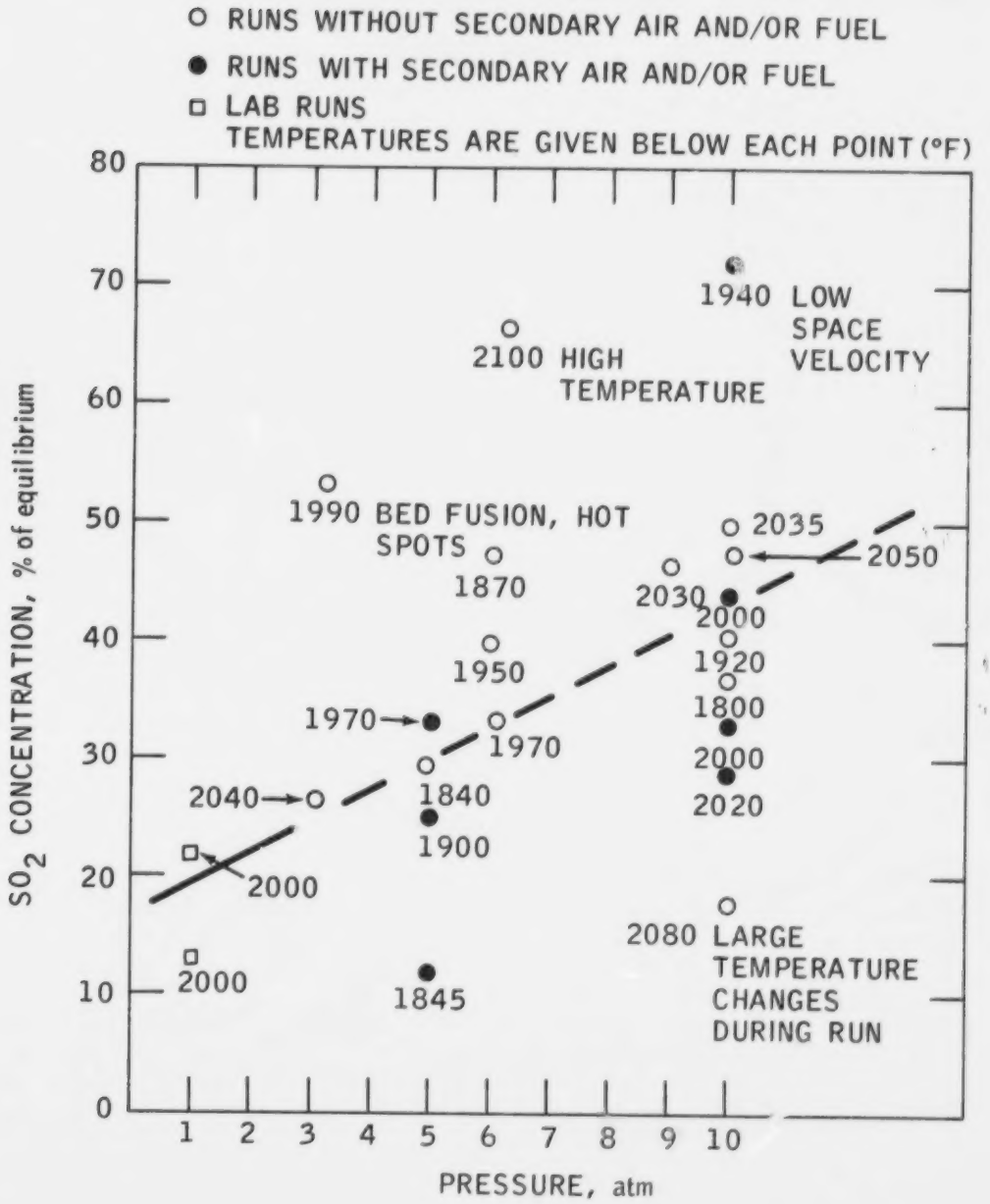


Figure 26

Regeneration studies - effect of pressure on SO_2 concentration

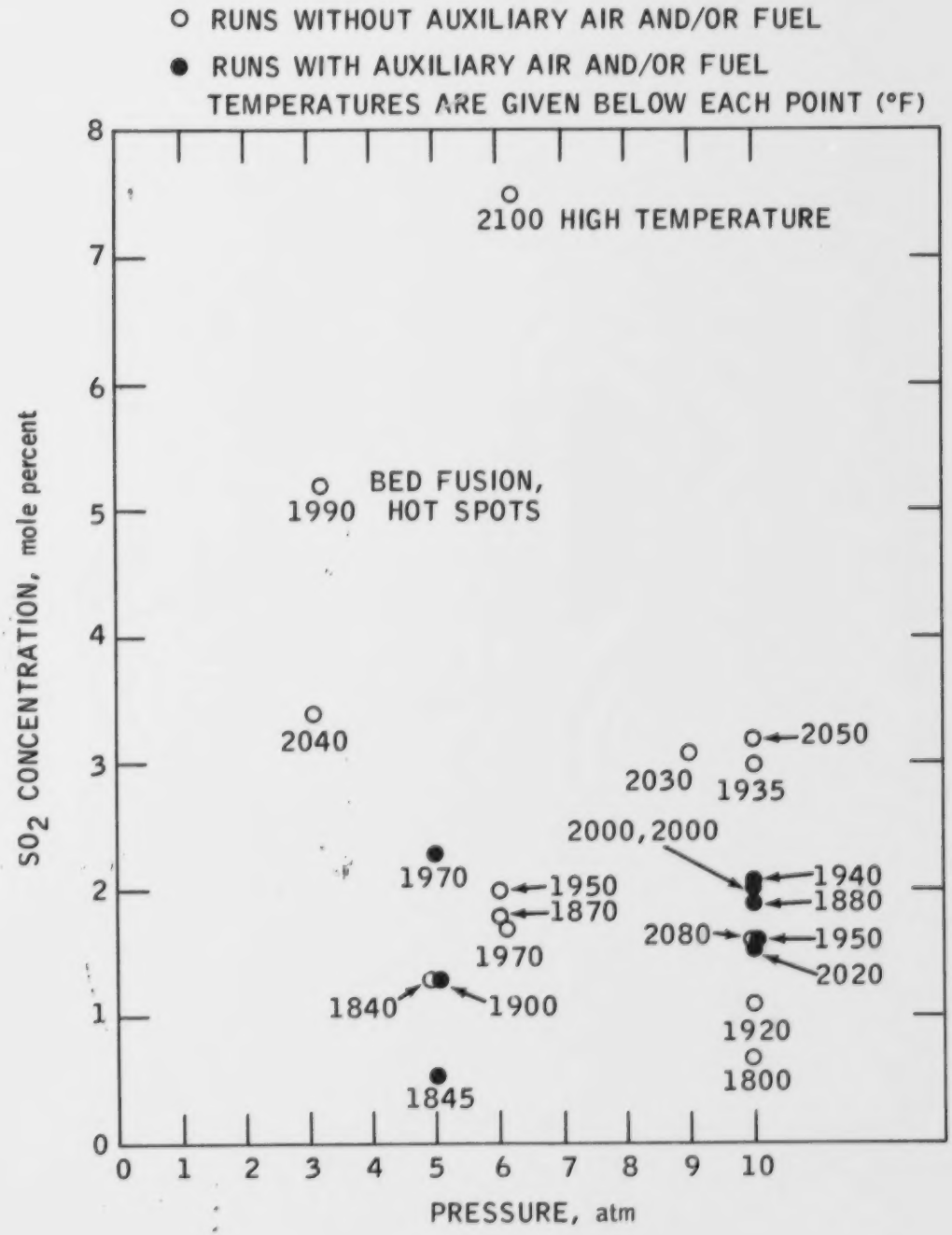
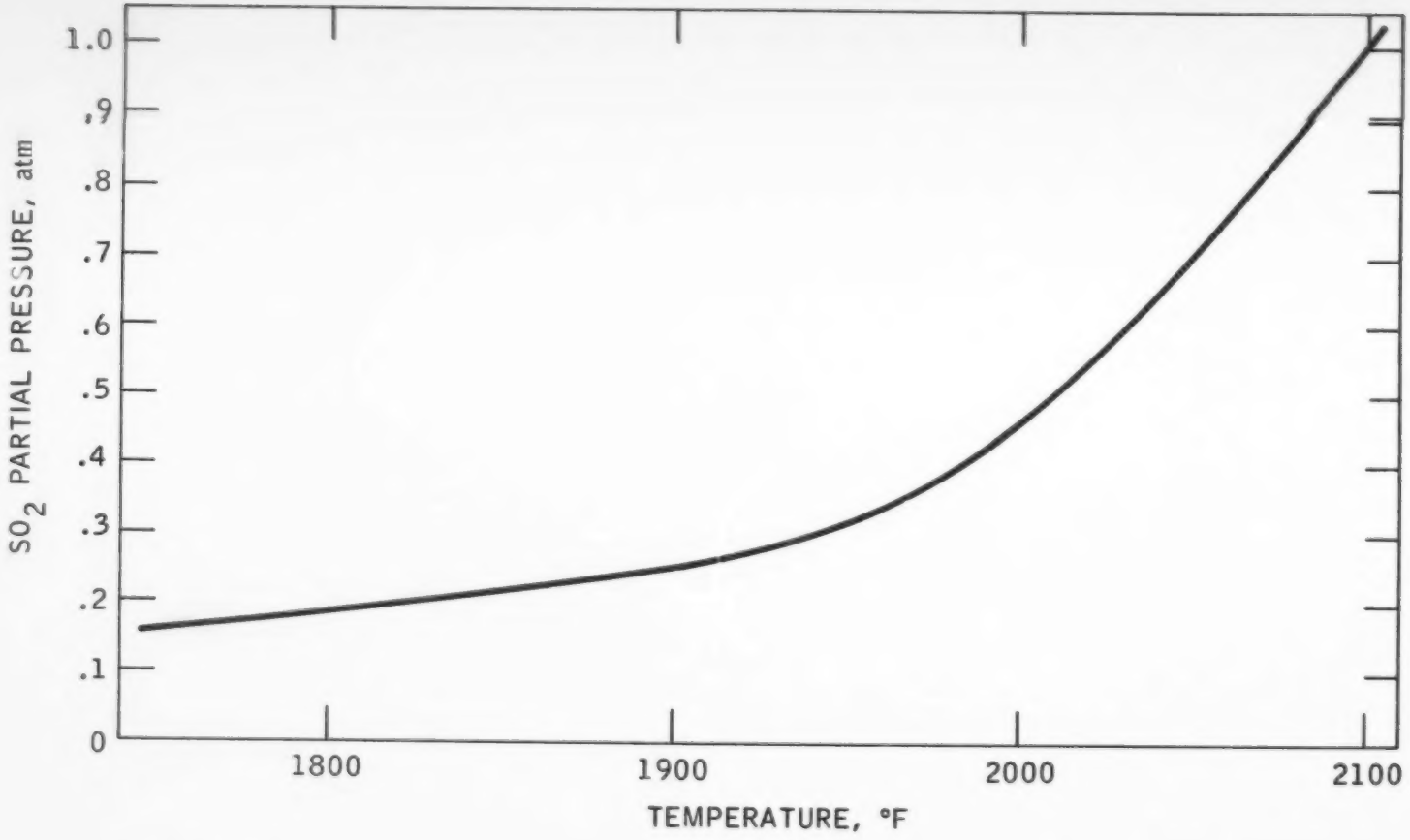


Figure 27

Regeneration studies - effect of temperature on SO_2 partial pressure at equilibrium



Runs made at temperatures below 1900°F generally resulted in low levels of SO_2 in the regenerator off-gas. For example, of four runs made at temperatures below 1875°F, only one resulted in an SO_2 concentration greater than 1.1% (volume) and two resulted in concentrations under 0.8%. On the other hand, for nine runs made in the temperature range 2000-2100°F, the lowest SO_2 concentration was 1.5% and five runs had average concentrations of over 2.0%. Figure 28 is a plot of mole percent of SO_2 vs. temperature. There is a definite trend toward higher SO_2 concentration at higher temperatures.

In addition to the molar or volume percentage of SO_2, the concentration of SO_2, expressed as a percent approach to equilibrium, also increased with temperature. Figure 29 is a plot of the percentage of equilibrium concentration vs. temperature. The figure shows a trend toward closer approach to equilibrium as temperature increases. This trend is more clearly seen if several data points are omitted (noted in figure).

Superficial Velocity and
Settled Bed Height

Varying superficial gas velocity and settled bed height can affect the concentration of SO_2 in the regenerator off-gas by changing both the contact time between gaseous and solid phases and the quality of fluidization. Decreasing the space velocity, e.g., by increasing bed depth, may not improve gas-solid contact if it causes a bed which is well fluidized to begin slugging. Space velocity can be defined as volumetric feed rate of gas based on average reactor conditions/volume of settled bed. It is equal to superficial velocity/settled bed height.

Most runs, as Table 12 shows, were made with a settled bed height of two feet. The greatest bed height used was 5.6 feet. Superficial velocities ranged from 1.8 to 5.4 feet/second. Space velocities, based on conditions inside the regenerator, ranged from 1850 to 7700 hr^{-1}. It is uncertain if changing settled bed height alone had a significant effect on the observed concentration of SO_2. Several earlier runs were made with different bed heights but these runs were characterized by poor fluidization, caused by melting and agglomeration of the bed. Thus, it is not possible to determine if different bed depths caused differences in results of these runs. It appears that a modest change in bed height affects regenerator preformance only to the extent that it affects quality of fluidization. The same can be said of superficial velocity.

Toward the end of work with the regenerator, evidence was obtained which indicated that reducing space velocity would improve performance. In run No. 124 (see Table 12), the reactor space velocity was decreased to about one-third of that of many previous runs. At an average bed temperature of 1940°F, the concentration of SO_2 was 2.0% or about 72% of equilibrium. This was a closer approach to equilibrium than was attained in any other run. From observations of the temperature

Figure 28

Regeneration studies - effect of temperature on SO_2 concentration

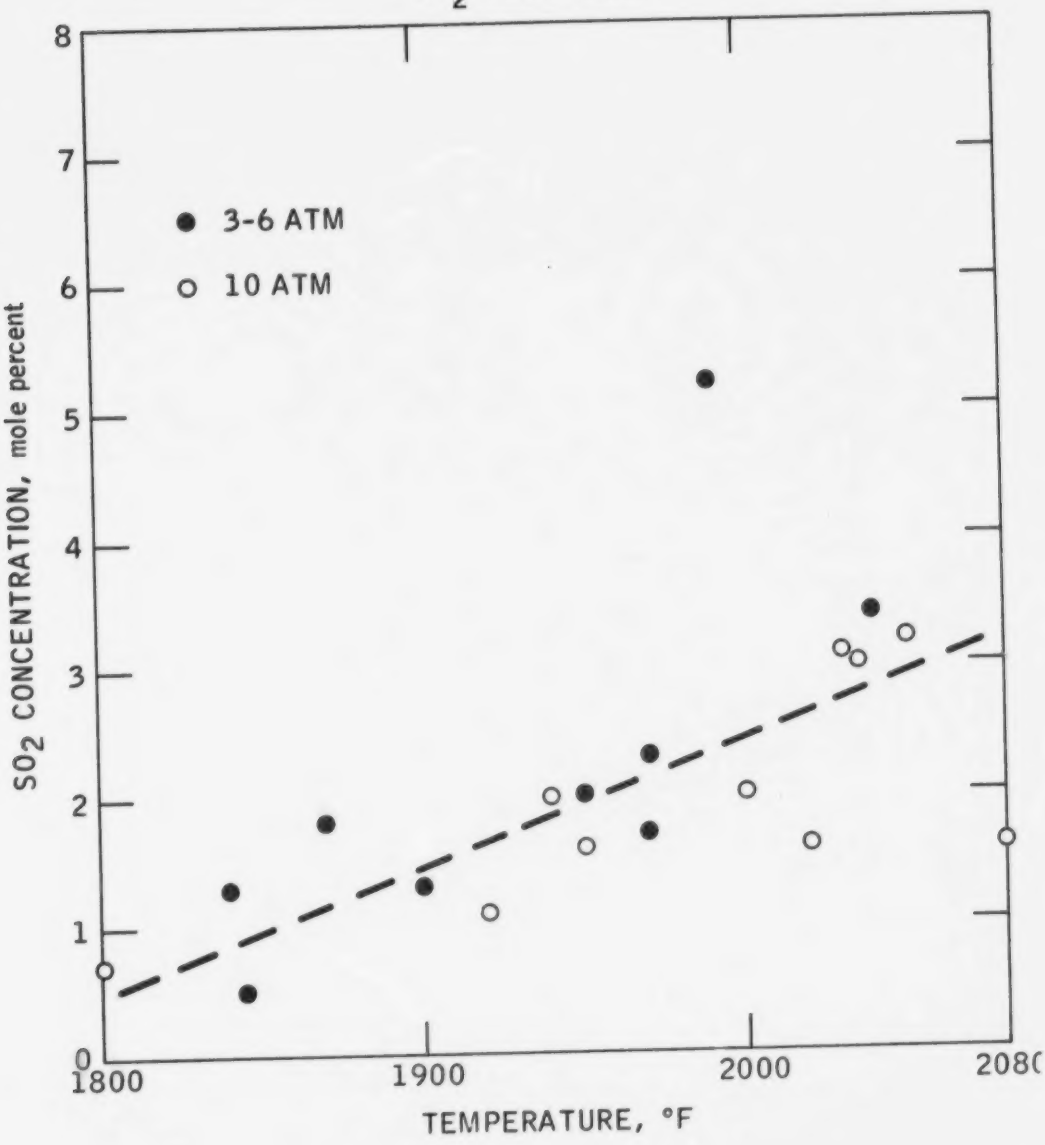
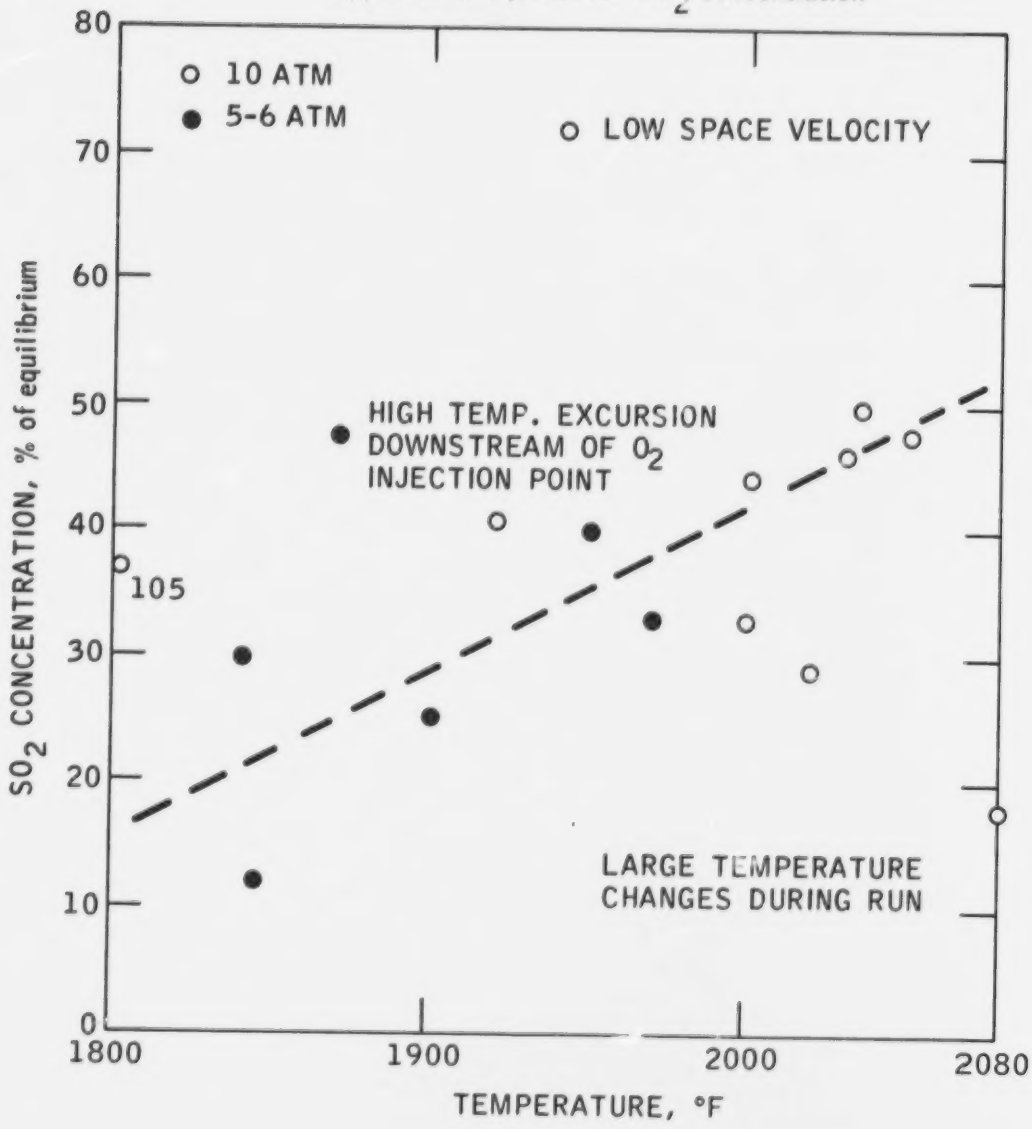


Figure 29

Regeneration studies - effect of temperature on approach to equilibrium SO_2 concentration



profile in the bed, it was believed that fluidization was not markedly different from earlier runs. Hence, the improvement in performance was attributed to an increase in gas-solid contact time.

Concentration of CO + H_2 in Reducing Gas

The air/fuel ratio determines the concentration of CO and H_2 in the reducing gas. The fuel used was a mixture containing 60 weight per cent propane (C_3H_8) and 40 weight per cent propylene (C_3H_6). A computer program (3) was used to estimate the air/fuel ratio necessary to give the desired concentration of CO + H_2. The program calculated equilibrium concentrations as a function of equivalence ratio, ϕ, defined as

$$\phi = \text{(air/fuel) stoichiometric/(air/fuel) operating}$$

An equivalence ratio of 1.4, for example, produces a gas product containing about 14% CO + H_2.

The percentage of CO + H_2 used in the reducing gas varied between 2 and 23%; however, the concentration most often used was about 15%. There appeared to be no significant effect of the concentration of reducing gas on the concentration of SO_2. Lower air/fuel ratios produce more CO + H_2 and consequently higher CO/CO_2 and H_2/H_2O ratios. However, there was insufficient data to determine whether increased CO/CO_2 and H_2/H_2O ratios caused increased formation of CaS as would be expected from equilibrium considerations.

Auxiliary Fuel

Run 120 (2020°F, 10 atm) was the first run made with a portion of the fuel added above the fluidizing grid, directly into the bed of solids. The remainder of the fuel and all of the air entered through the burner and produced a strongly oxidizing flame. Additional fuel added above the fluidizing grid produced a reducing gas containing approximately 10% CO + H_2.

Injection of fuel above the fluidizing grid significantly affected the temperature distribution in the bed. Thermocouples located at points 6, 12, and 18 inches above the grid indicated temperatures less than 10°F apart. This is a much closer distribution than was ever achieved without help from the electrical bed heaters, which were inoperative.

Not only is the uniformity of temperature significantly better when a portion of the fuel is burned in the bed, but combustion of fuel in this manner produces higher bed temperatures than introduction of the same amount of fuel into a burner located beneath the fluidizing grid. For example, run No. 123 (Table 12) was made at five atmospheres pressure with auxiliary fuel added 6 inches above the fluidizing grid (auxiliary air added 42 inches above grid). An object of this run was to determine

the maximum bed temperature that could be attained at five atmospheres pressure using auxiliary fuel and preheated air entering the burner. The temperature achieved was 1970°F. This compares to a bed temperature of 1840°F, attained in run No. 116, in which all of the fuel and air entered the burner, with none entering the bed. Moreover, the total flow of fuel was about 10% less in run No. 123 than in No. 116.

Another advantage of burning fuel directly in the bed is that the tendency of the bed to agglomerate is reduced. No melting or agglomeration of solids occurred in runs Nos. 120-124, made with auxiliary fuel, even though nitrogen was used to reduce the temperature of the burner flame in only two of these runs.

Auxiliary Air

A persistent problem with regeneration has been formation of large proportions of CaS, instead of CaO. Elemental sulfur and reduced sulfur compounds have also formed and an oxygen stream near the top of the regenerator (above the fluidized bed) was provided early in this work to oxidize these substances to SO_2. For run No. 119, this oxygen stream was removed and, instead, air was introduced into the bed at a point 12 inches above the fluidizing grid. The expectation was that any CaS which formed near the bottom of the bed would be oxidized to $CaSO_4$ or CaO upon contacting the air. Reducing gas was produced at the burner, in the usual manner. With good mixing in the fluidized bed, solids would be alternately exposed to strongly reducing and oxidizing (or midly reducing) environments. Unfortunately, something less than this could be expected to occur because mixing of solids in the regenerator is poor. Poor mixing was indicated in previous runs where the temperature distribution in the beds of solids was poor and also by results with the cold model test unit which showed that slugging of solids occurred, rather than uniform fluidization.

The results of run 119 (2000°F, 10 atm, air injected into bed) were different from most runs made previously at higher pressures. The average SO_2 concentration attained was 1.54% (corrected for dilution of the off-gas by N_2 which is present in the auxiliary air), or 33% of equilibrium, which is not unusual. However, the SO_2 concentration in the off-gas was nearly constant over the duration of the run. In previous work at 10 atm, the SO_2 concentration peaked sharply at the start of a run and continually decreased as the run progressed. An even more spectacular effect of auxiliary air was a sharp reduction in the amount of CaS formed during regeneration. Without auxiliary air, regenerated solids contained, typically, 40-70 mole percent CaS. With the addition of auxiliary air, the CaS content of solids was reduced to under one per cent in the majority of runs for which analyses were made. This is shown in Table 13.

Table 13. ANALYSIS OF SOLIDS FROM REGENERATION RUNS

Run No.	66-2690-98		66-2690-100		66-2690-101		66-2690-105	
Temp., °F	2010-2060		2080		1910-1940		1720-1880	
Pressure, atm.	9		10		10		10	
Sup. vel., ft./sec.	4.0		4.3		2.0		1.9	
% Stoich. air	66		66		67		69	
% Dil. N_2	16.3		16.7		20		16.7	
Set. bed ht., ft.	2		2		2		2	
Aux. air	NO		NO		NO		NO	
Aux. fuel	NO		NO		NO		NO	
Solids Composition	Mole %	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %	Wt. %
CaS	47.1	50.6	62.9	66.8	73.4	73.9	73.5	69.1
CaO	47.8	39.9	34.5	28.6	21.3	16.6	14.9	10.9
$CaSO_4$	3.2	6.5	0.8	1.6	3.4	6.5	9.6	17.1
$CaCO_3 + CaSO_3$	<1.8	<3.0	<1.8	<3.0	<1.9	<3.0	<2.0	<2.9

Run No.	66-2690-115		66-2690-116		66-2690-119		66-2690-120	
Temp., °F	2050		1840		2000		2020	
Pressure, atm.	10		4.9		10		10	
Sup. vel., ft./sec.	3.6		4.1		3.7		3.8	
% Stoich. air	77		70		78		79	
% Dil. N_2	0		0		5		0	
Set. bed ht., ft.	2		2		2		2	
Aux. air	NO		NO		12 in. above grid		NO[b]	
Aux. fuel	NO		NO		NO		6 in. above grid	
Solids composition	Mole %	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %	Wt. %
CaS	41.3	45.2	57.7	60.5	0.2	0.2	0.7	0.9
CaO	54.7	46.6	38.0	31.0	98.4	96.5	95.2	89.7
$CaSO_4$	4.0	8.2	4.3	8.5	1.4	3.3	4.1	9.4
$CaCO_3 + CaSO_3$	a							

Table 13 (continued). ANALYSIS OF SOLIDS FROM REGENERATION RUNS

Run No.	66-2690-122b		66-2690-123	
Temp., °F	2000		1970	
Pressure, atm.	10		5	
Sup. vel., ft./sec.	2.8		4.0	
% Stoich. air	72		72	
% Dil. N_2	0		0	
Set. bed ht., ft.	2		2	
Aux. air	42 in. above grid		42 in. above grid	
Aux. fuel	6 in. above grid		6 in. above grid	
Solids composition	Mole %	Wt. %	Mole %	Wt. %
CaS	8.3	10.0	0.2	0.3
CaO	88.5	82.8	98.1	95.7
$CaSO_4$	3.2	7.2	1.7	4.0
$CaCO_3 + CaSO_3$	a			

[a] Negligible
[b] Solids exposed to oxidizing mixture (107% stoich. air) for several minutes after run.

Particle Size

All but one run was made with -10 + 20 mesh material. To test the effect of particle size, run No. 126 was made with -20 + 40 mesh Drierite. Unfortunately, problems with equipment necessitated a shutdown several minutes after the start of regeneration. The unit was restarted several days later with the bed still in place. The temperature profile in the bed indicated poor fluidization. It is probable that moisture condensing in the reactor during pre-heating had caused some of the bed to agglomerate. Hot spots developed and the run had to be terminated. Average bed temperature was 1880 $\pm$ 80°F. Examination of solids indicated that the bed had agglomerated but little fusion had taken place.

The average concentration of SO_2 in the off-gas was 1.2% although a peak concentration of 1.9% (corrected for N_2 addition in auxiliary air) was observed. Based on an average bed temperature of 1880°F, these levels represent approaches of 50 and 70 percent, respectively. However, when the uncertainty in the average bed temperature is taken into account, the approach to equilibrium could be anywhere in the range of 35-100 percent. Hence, it cannot be clearly determined if SO_2 concentration was increased by reducing particle size. Nevertheless, if poor fluidization is taken into account, an approach to equilibrium of only 35% still appears high when compared to other runs in which agglomeration of the bed had occurred.

Use of Sulfated Limestone

Drierite was the bed material for all runs except No. 125, in which -10 + 20 mesh sulfated limestone from the Bureau of Mines was used. Early in the run, a hot spot developed near the point at which secondary air entered the bed. For a brief period, temperatures at this position approached 2370°F. The temperature profile in the bed was much poorer than usually observed with Drierite. In addition, a poor temperature profile was noted when the bed was preheated prior to regeneration.

Examination of solids showed that much of the bed had agglomerated in the reactor. Fused pieces which were quite hard were also found. It is likely that the bed had begun to agglomerate at the outset of the run (possibly during preheating). Diluent nitrogen was introduced early in the run; however, by this time, high bed temperatures were already observed. The average SO_2 concentration was only 0.62% although a peak concentration of 1.57% was observed, which corresponds to 52% of equilibrium.

Quality of Fluidization

Quality of fluidization is probably the most poorly controlled and most difficult to evaluate of all factors which affect performance of the regenerator. The best means available to determine how well solids

were fluidized was to check the closeness of the temperature distribution in the bed. In several runs, where solids agglomerated, temperature differences across the bed were as high as 500°F. A typical span in temperature for beds in which no agglomeration occurred was 150°F. Where auxiliary fuel was used, a spread in temperature of 50°F was common, but the improvement in temperature distribution was probably caused by the additonal fuel and not by better fluidization.

Analysis of Solids

Solids from some regeneration runs were analyzed for $CaSO_4$, CaO, CaS, $CaCO_3$, and $CaSO_3$. The analytical techniques that were used are given in the Appendix. Table 13 gives results of the analyses. No significant amounts of $CaCO_3$ or $CaSO_3$ were found. The amount of unconverted $CaSO_4$ was usually small. Run Nos. 119, 122b, and 123 were made with auxiliary air; solids from these runs had levels of CaS which were sharply lower than solids from runs made without auxiliary air.

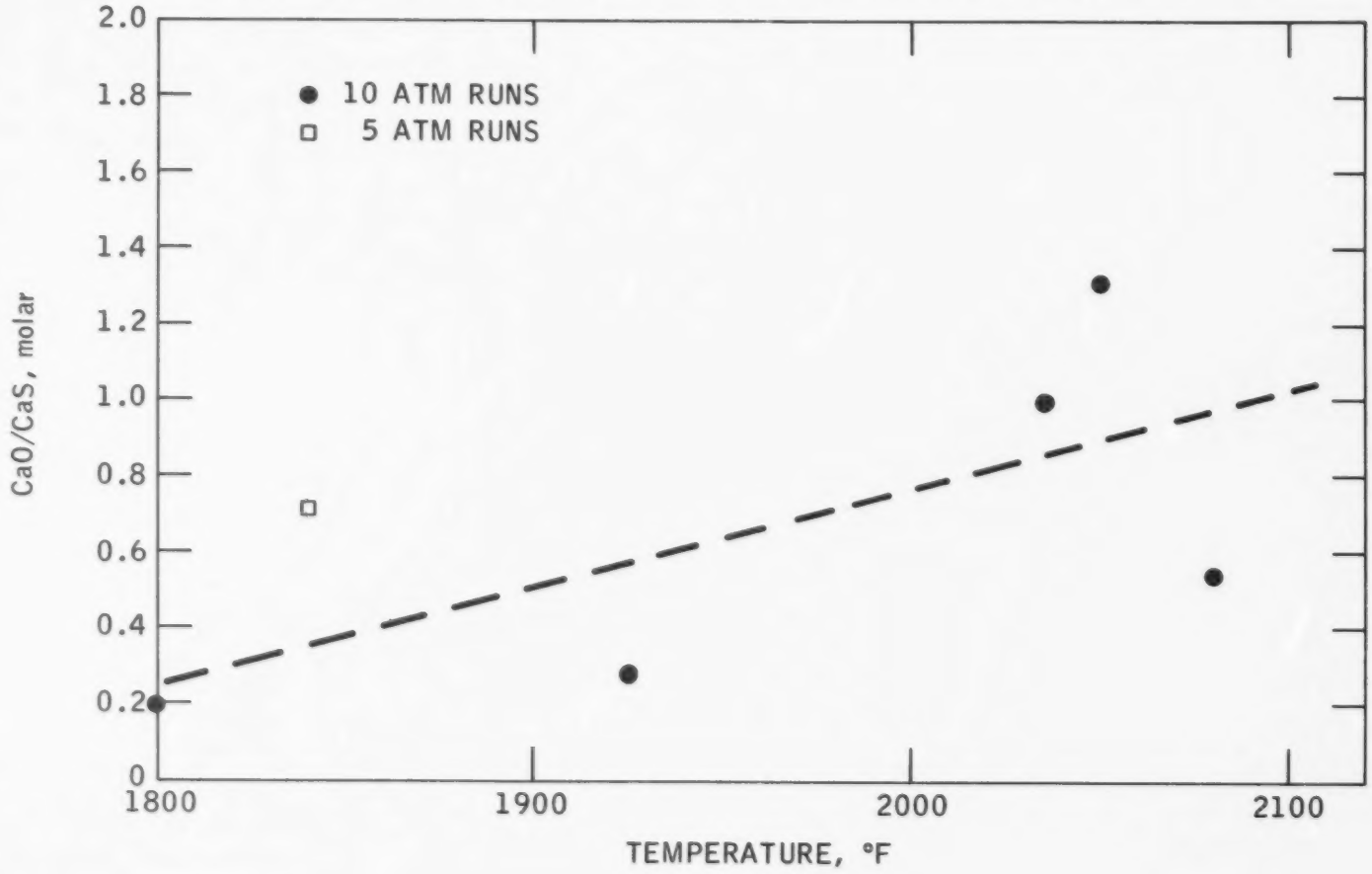
Figure 30 is a plot of the molar ratio of CaO/CaS vs. temperature for runs made without auxiliary air. Increased temperatures appear to favor higher CaO/CaS ratios. All data except for run 116 are for ten atm. pressure. Run 116, made at five atm, has a higher CaO/CaS ratio than would be expected at this temperature from data at ten atmospheres. This might indicate that reduced pressure favors higher CaO/CaS ratios.

Attrition

Attrition in the batch fluidized bed regenerator was very low, typically 1-2% of the weight of Drierite charged.

Figure 30

Regeneration studies - effect of temperature on CaO/CaS ratio in regenerated solids



SECTION VII

DISCUSSION OF RESULTS

REGENERATION STUDIES

The SO_2 concentration measured in the product gas at 10 atm pressure averaged about 2%. This corresponds to 40 to 50% of the concentration calculated if the gas and solids were in chemical equilibrium. This suggests that the SO_2 concentration is limited by reaction rates. This is supported further by data which indicate that higher temperatures, higher pressures, longer gas/solid residence times and possibly smaller solids particles give SO_2 concentrations which are closer to the calculated equilibrium levels. The reaction rates can be increased by any number of changes in operating conditions. However, only a few of these options are open because of certain practical limitations. The two most likely ways of improving the conversion of $CaSO_4$ to SO_2 and CaO are to increase the overall residence time and to improve the gas/solids residence time distribution by improving the quality of fluidzation.

For a given regenerator vessel diameter, the best way to increase the residence time is to decrease the gas linear velocity. However, for a given SO_2 production rate, a larger diameter regenerator vessel with an increased inventory of solids would be required. Increasing the residence time by increasing bed depth is not as attractive since the bed pressure drop would be increased, solids entrainment from the regenerator would be increased and the quality of fluidization would probably be poorer, giving a less favorable residence time distribution. Improvements in the residence time distribution could be made by optimizing the distributor design and also using shallower beds. The use of baffles to promote better fluidization does not appear to be as likely since the very high temperatures occurring in the regenerator pose a materials problem. Also, if the bed were to agglomerate, baffles would complicate the job of cleaning out the bed.

Other ways of increasing the SO_2 concentration in the regenerator off gas do not appear to be promising. For example, higher temperatures will increase the probability of bed agglomeration, especially when fly ash carried over from the combustor is present. Higher pressures may increase the rate, but decrease the equilibrium concentration of SO_2, so the net effect is small or negative. Using smaller particles does not appear practical since it would require a larger combustor diameter to prevent excessive solids entrainment. Dropping pressure to 1 to 2 atm will result in an increase in SO_2 concentration by making the equilibrium more favorable, even if rates are decreased. However, this would require operating the regenerator at a lower pressure than the combustor, and development of high temperature lock hoppers and valves would be necessary. In addition, it may not be possible to provide enough thermal energy in the hot reducing gases fed to the

regenerator to carry out the regeneration at low pressure without diluting the product gas and decreasing the SO_2 concentration. If this is the case, the SO_2 product concentration could be limited by the amount of feed gas required to provide the needed energy and not by either chemical equilibrium or reaction rates. Operating at lower pressure would also require higher fluidizing velocities and/or larger reactor diameters.

Introduction of auxiliary air directly into the regenerator bed promotes high conversion of $CaSO_4$ to CaO with very little CaS formation. It is believed that air injection creates an oxidizing zone in the bed above the reducing zone. The solids move back and forth between the zones so that CaS formed in the reducing zone by over-reduction of $CaSO_4$ can be oxidized back to $CaSO_4$ or directly to CaO and SO_2 in the oxidizing zone. This ultimately gives high conversion of $CaSO_4$ and high selectivity to CaO.

Injection of at least a portion of the fuel directly into the bed also improves operation by providing higher and more uniform bed temperatures. There was also less tendency to agglomerate the bed when direct injection was used. Higher bed temperatures are due to less heat losses compared to the case where all fuel is burned in an adjacent burner zone. Burning part of the fuel in the bed also causes the thermal energy to be released over a greater volume and in direct contact with the bed solids. This promotes more uniform bed temperatures and probably results in the transfer of energy between the gas and solids at a lower gas temperature. This, in turn, decreases the chance for localized overheating of solids which can cause solids to soften and agglomerate.

The best method of operating the regenerator appears to be to add both auxiliary air and part of the fuel to the bed at separate points. The optimum split between air and fuel added to the burner and directly to the bed and the location of the injection points must be determined.

COMBUSTION STUDIES

Initial SO_2 removal of about 85% has been measured with both -7 mesh calcined limestone and half-calcined dolomite at combustion pressures of 5-8 atm. However, the runs were too short to draw any general conclusions about the suitability of either sorbent at these conditions. Also, the Tymochtee dolomite showed very high attrition rates. Unless this is related somehow to the equipment or the manner in which the dolomite was used, it would appear to rule out the use of Tymochtee dolomite in a once through operation.

The NO levels measured in the flue gas are very high considering the high combustion pressures. However, because coal feeding was very erratic during the runs, the excess air level was much higher than planned. It is believed that high NO emissions were due to the high oxygen levels in the bed.

After resolving the coal feeding problem, the combustion program will continue testing other sorbents and measuring the effects of operating conditions on SO_2 and NO emissions.

EQUIPMENT DEVELOPMENT

Development of equipment became a significant part of the experimental program. The use of high temperature ceramic materials in the regenerator did not prove successful due to poor resistance to thermal shock and reaction with molten bed material. Water cooled stainless steel components performed very well under the same conditions.

A burner was developed in this study to heat and provide reducing gas feed for the regenerator and also to preheat the combustor. This burner proved to be very versatile, operating over a wide range of pressures, oxidizing and reducing conditions and flow rates.

Coal feeding at pressures up to 10 atm is possible with a modified Petrocarb injector, but careful attention must be paid to the operation to prevent plugging. Close control of the pressure differential between the injector and the combustor, the flow of injection air, lack of sharp bends or corners in the transfer line and coal particle size and dryness must be maintained. Some problems still remain in the proper design and location of the coal probe which injects the coal into the hot combustor.

The continuous transfer of solids between the combustor and regenerator by the use of gas pulses is feasible. The system works well at ambient temperature and based on other studies (4) should work even better at higher temperatures due to increased gas viscosity.

SECTION VIII

PROGRAM FOR OPERATION OF MINIPLANT

The overall objective of the Miniplant program is to demonstrate the continuous fluidized bed combustion process at conditions anticipated for commercial plants. The specific objectives are to

- Verify the reductions in SO_2 emissions
- Measure the reduction in NO_x emissions
- Verify particulate loadings in the flue gas
- Measure erosion of a stationary target simulating a turbine blade surface in the flue gas
- Test various coals in combination with various sorbents (limestones, dolomites). Select sorbents, based on location, suitable for the 30MW demonstration unit
- Verify overall operability of the continuous system including turndown ratio and methods
- Test and develop (if necessary) system components
- Measure, verify and/or demonstrate other items needed for the design and operation of the 30MW demonstration unit

At the present time, no plans are being made to operate the regenerator section of the Miniplant. Therefore the operation will be based on the once-through use of sorbent. The primary operating variables whose effects will be studied are: combustion pressure and temperature, sorbent/coal feed ratio, coal and sorbent type. Other variables which cannot be as readily changed or whose effects may be less will be studied to a lesser extent. These are: fluidized bed level, coal and sorbent particle size, excess oxygen in the flue gas and coal rate. Fluidizing velocity is fixed by the coal rate and excess oxygen.

The primary measured quantities will be:

- Flue gas composition
- Used solids composition
- Temperature distribution in the bed
- Solids loss and particle size change

- Corrosion and erosion effects including the effects on the stationary test piece in the flue gas
- Burning front location by measurement of intra bed gas compositions
- Overall system response to changes in operating conditions, including response to turndown and turnup measures
- General equipment performance

From these measurements, the following will be calculated:

- Fraction SO_2 reduction
- Combustion efficiency
- Heat transfer coefficients
- Fraction of bed attrited
- Heat losses

The initial operation of the combustor will consist of testing various coal and sorbent combinations. Because of the somewhat limited objectives of this initial study, only the effects of the primary operating variables will be studied, the other variables will be fixed. The run plan will consist of a block of eight runs for each sorbent and coal combination. The runs will be as follows:

Temp (°F)	Ca/S Mole/Mole	Press (atm)
1500	2/1	10
1600	2/1	10
1700	2/1	10
1700	4/1	10
1500	4/1	10
1600	4/1	10
1600	3/1	10
1600	3/1	5

The sorbents and coals tested will be chosen in cooperation with the EPA. The choice will depend on the results of current experimental studies sponsored by the EPA and the location of the 30MW demonstration plant. Other test conditions, such as the possible use of precalcined sorbent, will be set before the tests begin.

After the initial program has been completed, the program will be directed toward solution of problems which become evident during the initial program. At this time, the effect of the secondary variables can also be studied if warranted. Another option would be to study regeneration of sulfated sorbent, if that appears to be warranted at that time.

SECTION IX

REFERENCES

1. Jonke, A. A., et al., Reduction of Atmospheric Pollution by the Application of Fluidized Bed Combustion. Argonne National Laboratory, Monthly Progress Reports 32-35, June - September 1971.

2. Zenz, F. A., and Othmer, D. F., Fluidization and Fluid Particle Systems, Reinhold Publishing Corporation, 1960, p. 136-174, 313-350.

3. Gordon, S., and McBride, B., Chemical Equilibrium Program. NASA Lewis Research Center, November 1970.

4. Craig, J. W. T., et al., Study of Chemically Active Fluid Bed Gasifier for Reduction of Sulphur Oxide Emissions. Final Report OAP Contract CPA 70-46, Esso Petroleum Co., June 1972.

ADDITION REFERENCES

5. Archer, D. H., et al, Evaluation of the Fluidized Bed Combustion Process, Vol. I, II, III, Westinghouse Research Laboratories, November 1971.

6. Hammons, G. A., and Skopp, A., A Regenerative Limestone Process for Fluidized Bed Coal Combustion and Desulfurization, Esso Research and Engineering Co., February 28, 1971.

7. Skopp A., et al., Studies of the Fluidized Lime-Bed Coal Combustion Desulfurization System, Esso Research and Engineering Company, December 31, 1971.

SECTION X

LIST OF PUBLICATIONS

1. Hoke, R. C., Shaw, H., and Skopp, A., A Regenerative Limestone Process for Fluidized Bed Coal Combustion and Desulfurization. Presented at the Third International Conference on Fluidized Bed Combustion, College Corner, Ohio, October 29 - November 1, 1972.

2. Bertrand, R. R., Hoke, R. C., Shaw, H., and Skopp, A., Combustion of Coal in a Bed of Fluidized Lime. Presented at the American Chemical Society National Meeting, Chicago, Illinois, August 26-31, 1973, also submitted for publication in Hydrocarbon Processing.

3. Hoke, R. C., Fluidized Bed Combustion of Solid and Liquid Fuels. Presented at the Symposium on Modern Developments in Combustion Technology, Pennsylvania State University, August 1, 1973.

PATENT MEMORANDA SUBMITTED

1. Ruth, L. A., Hoke, R. C., Reduction of $CaSO_4$ by direct injection of fuel into a fluidized bed.

2. Hoke, R. C., Vath, E. C., Removal of SO_2 from flue gas followed by sulfite precipitation.

3. Ruth, L. A., Shaw, H., Vath, E. C., High pressure gas generating burner.

SECTION XI

GLOSSARY

Abbreviation	Definition
atm	atmosphere - unit of pressure
BTU	British Thermal Unit
CMTU	Cold Model Test Unit
dia.	diameter
d/p	differential pressure
Δp	pressure difference
ΔT	temperature difference
^{o}F	degree Fahrenheit
F	coal feed rate, lb/hr
FRC	flow recorder controller
ft.	foot
gm.	gram
hr.	hour
I.D.	internal diameter
IR	infra-red
Kw	kilowatt
lb.	pound
min.	minute
NDIR	non dispersive infra-red
O.D.	outside diameter
P	pressure in coal receiving vessel, psig
ppm	parts per million
PRC	pressure recorder controller

psi	pounds per square inch
psia	pounds per square inch absolute
psig	pounds per square inch gage
R	injection air rotameter setting, % of scale
SCFM	standard cubic feet per minute
sec.	second
sq. ft.	square feet
wt.	weight
ϕ	equivalence ratio
μ	micron - unit of length

Conversion Factors - English to Metric Units

	English system	Metric equivalent
Length	inch	2.54 centimeter
	foot	0.305 meter
Area	square foot	0.093 square meter
Volume	gallon	3.785 liter
	cubic feet	38.32 liters
Mass	pound	453.6 grams
Pressure	pound per square inch	51.70 millimeters Hg
	atmosphere	760 millimeters Hg
Temperature	° Fahrenheit	1.8 (°Celsius) + 32
Energy	British thermal unit	252 calories

SECTION XII

APPENDIX

TECHNIQUES FOR ANALYSIS OF SOLIDS

Solids from some regeneration runs were analyzed for $CaSO_4$, CaO, CaS, $CaCO_3$, and $CaSO_3$. The analytical techniques that were used are described below.

SO_4^{-2} - The sample was treated with acidic $BaCl_2$ solution. The $BaSO_4$ precipitate was weighed.

CO_3^{-2} - Acidic H_2O_2 was added to the sample. The solution was stripped with N_2 and the gas passed through H_2O_2/H_2SO_4, Drierite, $CuSO_4$, and Ascarite. CO_3^{-2} was determined from the weight gain of the Ascarite.

Ca^{+2} - Ca^{+2} was determined by atomic absorption.

SO_3^{-2} - The sample was treated overnight with $HgCl_2$, then heated with acid and stripped with N_2. The gas was passed through excess I_2, $S_2O_3^{-2}$, and H_2O. The scrubbers were combined and the solution back titrated with $S_2O_3^{-2}$. SO_3^{-2} was determined from I_2 consumed.

S^{-2} - Since no SO_3^{-2} was found, the sample was treated with acidic I_2 and the excess I_2 titrated with $S_2O_3^{-2}$. S^{-2} was determined from I_2 consumed.

O^{-2} - CaO was determined by difference. The excess number of moles of calcium over the moles of anions was assumed to correspond to O^{-2}.

Table A-1. FIXED BED SIMULATED COMBUSTION RUNS

Bed Mat'l.	Temp., °F	Press., psig	Gas rate, SCFM	Feed gas comp.				Prod. gas comp.				Conv., % of	
				CO, ppm	NO, ppm	CO_2, %	O_2, %	CO, ppm	NO, ppm	CO_2, %	O_2, %	CO	NO
Limestone 1359[a]	1600	0	0.11	945	1400	--	--	10	400	--	--	99	71
	1600	0	0.10	988	862	17	--	770	635	17	--	22	26
	1700	0	0.10	988	862	17	--	800	625	17	--	19	27
	1700	0	0.10	1870	1800	--	--	160	22	--	--	92	99
	1600	135	0.10	985	893	18	--	300	165	13	--	70	82
	1600	135	0.10	1870	1800	--	--	160	23	--	--	91	99
	1600	135	0.10	900	1400	--	--	10	375	--	--	99	73
Dolomite 1337[b]	1600	0	0.1	900	1400	--	--	20	350	--	--	98	75
	1600	135	0.1	900	1400	--	--	10	280	--	--	99	80
	1600	0	0.1	983	840	16	--	830	680	17	--	16	19
	1600	135	0.1	983	840	16	--	270	105	13	--	73	88
	1600	135	0.10	1080	978	15	2.3	100	112	16	2.3	91	89
	1600	135	0.10	2080	1987	--	--	85	180	--	--	96	91
	1600	0	0.10	2080	1987	--	--	95	243	--	--	95	88

Table A-1 (continued). FIXED BED SIMULATED COMBUSTION RUNS

Bed Mat'l.	Temp., °F	Press., psig	Gas rate, SCFM	Feed gas comp.				Prod. gas comp.				Conv., % of	
				CO, ppm	NO, ppm	CO_2, %	O_2, %	CO, ppm	NO, ppm	CO_2, %	O_2, %	CO	NO
Limestone 1359[a]	1600	135	0.10	1245	1150	12.7	--	330	355	15.2	--	74	69
	1400	135	0.82	1245	1150	12.7	--	1055	965	15.7	--	15	16
	1600	135	0.40	1245	1150	12.7	--	990	888	15.7	--	20	23
	1600	135	0.55	1245	1150	12.7	--	1040	905	15.7	--	16	21
	1550	135	0.70	1245	1150	12.7	--	1080	940	15.7	--	13	18
	1520	135	0.66	1245	1150	12.7	--	1095	935	15.7	--	12	19
	1600	135	0.10	2080	1987	--	--	155	177	--	--	93	91
	1600	135	0.10	1080	987	15.2	2.3	255	115	15.6	2.2	76	88
	1600	135	0.10	1060	972	16.3	2.4	50	90	16.8	2.5	95	91
	1600	135	0.10	2080	1987	--	--	38	163	--	--	98	92
	1600	135	0.10	1245	1150	12.7	--	205	300	15.5	--	84	74
	1600	135	0.55	1245	1150	12.7	--	890	840	15.5	--	28	27
	1 00	135	0.10	965	978	--	--	0	100	--	--	100	90

[a] -18+20 mesh, calcined.
[b] -16+25 mesh, calcined.

Table A-2. AIR, FUEL AND SOLIDS INPUTS FOR REGENERATION RUNS

Run No.	Charge material, weight, lbs.	Input in SCFM					
		Fuel	Air	Aux. fuel	Aux. air	N_2	O_2[a]
66-2690- 71	Drierite, 9.2	0.21	5.0[b]	--	--	0.67	0.83
72	Drierite, 18.4	0.32	4.9[b]	--	--	0.64	0.80
75	Drierite, 9.8	1.11	20.8	--	--	--	2.34
78	Drierite, 13.1	0.46	8.4	--	--	--	0.98
86	Drierite, 13.1	0.52	8.4	--	--	--	1.00
89	Drierite, 13.1	0.53	8.9	--	--	--	0.76
98	Drierite, 6.6	1.35	20.5	--	--	3.98	2.48
100	Drierite, 6.6	1.58	24.0	--	--	4.80	2.98
101	Drierite, 6.6	0.75	11.6	--	--	2.85	2.30
105	Drierite, 6.6	0.73	11.6	--	--	2.33	2.30
109	Drierite, 6.6	1.23	24.0	--	--	--	2.4
115	Drierite, 6.6	1.38	24.3	--	--	--	2.2
116	Drierite, 6.6	0.93	15.0	--	--	--	2.2
119	Drierite, 6.6	1.00	18.0	--	3.46-7.52	0.82-2.32	--
120	Drierite, 6.6	0.92	26.3	0.53-0.92	--	0-2.63	--
121	Drierite, 6.6	0.42	11.6	0.21-0.33	2.42-4.26	--	--
122A	Drierite, 6.6	0.36	9.6	0.22	3.46-4.34	--	--
122B	Drierite, 6.6	0.74	19.4	0.44	7.84-8.95	--	--
123	Drierite, 6.6	0.45	13.8	0.38	2.42-6.28	--	--
124	Drierite, 13.2	0.61	17.8	0.63-0.82	3.5-7.0	--	--
125	sulfated limestone, 9.35	1.2	20.0	0.12	7.4	2.7	--
126	Drierite[c], 15.6	0.7	21.0	0.1	7.0	--	--

[a] Injected above bed to prevent sulfur deposition in exit lines.
[b] 0.17 SCFM CO_2 also added.
[c] -20+40 mesh; -10+20 mesh used in all other runs.

Table A-3. COMPOSITION OF EFFLUENT STREAM FOR REGENERATION RUNS

Run No.	Component, molar % or ppm[a]											
	SO_2, %		CO, ppm		CO_2, %		H_2O, %		O_2, %	N_2, %[b]		NO, ppm	
66-2690- 71	3.04	3.37[c]	1570	1740[c]	11.6	12.9[c]	10.6	11.7[c]	9.83	64.8	71.8[c]	125	139[c]
72	4.78	5.23	1750	1910	13.7	14.9	14.6	16.0	8.54	58.2	63.7	150	164
75	6.94	7.52	2360	2560	14.7	16.0	14.3	15.5	7.71	56.1	60.8	260	280
78	1.81	2.01	2590	2900	12.3	13.7	15.2	16.9	9.87	60.5	67.2	--	--
86	1.58	1.79	3630	4130	14.0	15.9	14.7	16.7	11.9	57.4	65.2	--	--
89	1.56	1.73	3000	3320	15.6	17.3	21.9	23.5	9.9	50.7	56.3	--	--
98	3.0	3.1	1200	1230	12.5	12.8	14.6	15.0	2.5	66.9	68.6	--	--
100	1.5	1.6	--	--	14.9	15.7	15.0	15.8	4.8	63.8	67.0	--	--
101	1.0	1.1	--	--	12.7	14.4	13.5	15.3	12.0	60.8	69.0	--	--
105	0.6	1.1	--	--	14.8	16.9	11.9	13.6	12.5	60.2	68.4	--	--
109	2.8	3.0	--	--	13.0	14.0	13.0	14.0[d]	7.0	64.2	69.0	--	--
115	1.8	1.9	--	--	13.3	14.1	15.7	16.7[d]	5.8	63.4	67.3	160	170
116	0.96	1.07	--	--	13.7	15.2	13.0	14.4	10.0	62.1	68.5	210	230
119	1.30	1.54	630	750	14.1	16.7	12.0	14.2	<1	72.6	67.6	190	220
120	1.57	1.57	9000	--	15.2	--	13.0	--	<1	69.3	--	180	--
121	1.05	1.29	870	1070	13.1	16.1	12.7	15.6	<1	73.2	67.0	105	130
122A	0.44	0.54	17	21	11.8	14.6	12.6	15.6	<1	75.2	69.3	100	120
122B	1.60	2.02	61	77	12.7	16.0	12.4	15.6	<1	73.3	66.4	110	140
123	1.90	2.30	260	310	10.5	12.5	15.0	17.9	<1	72.6	67.3	100	120
124	1.67	2.05	880	1080	16.7	20.5	12.3	15.1[d]	<1	69.3	62.3	110	140
125	0.42	0.62	2.0%	2.5%	12.0	14.9	15.6	19.5[d]	<1	70.0	62.5	110	140
126	1.0	1.2	0.8%	1.0%	13.0	15.9	13.9	17.0[d]	--	71.3	64.9	190	230

[a] Concentrations have been corrected for condensation of water prior to analysis.
[b] Found by difference.
[c] Second column gives concentrations corrected also for injection of oxygen above bed OR addition of N_2 which is contained in auxiliary air.
[d] Calculated. Water not measured.